IGC HK EXAM - WJEC

WJEC & Eduqas - Chemistry

Mock 1 Practice Paper

16 Azomethane, $CH_3N_2CH_3$, decomposes to form nitrogen and ethane.

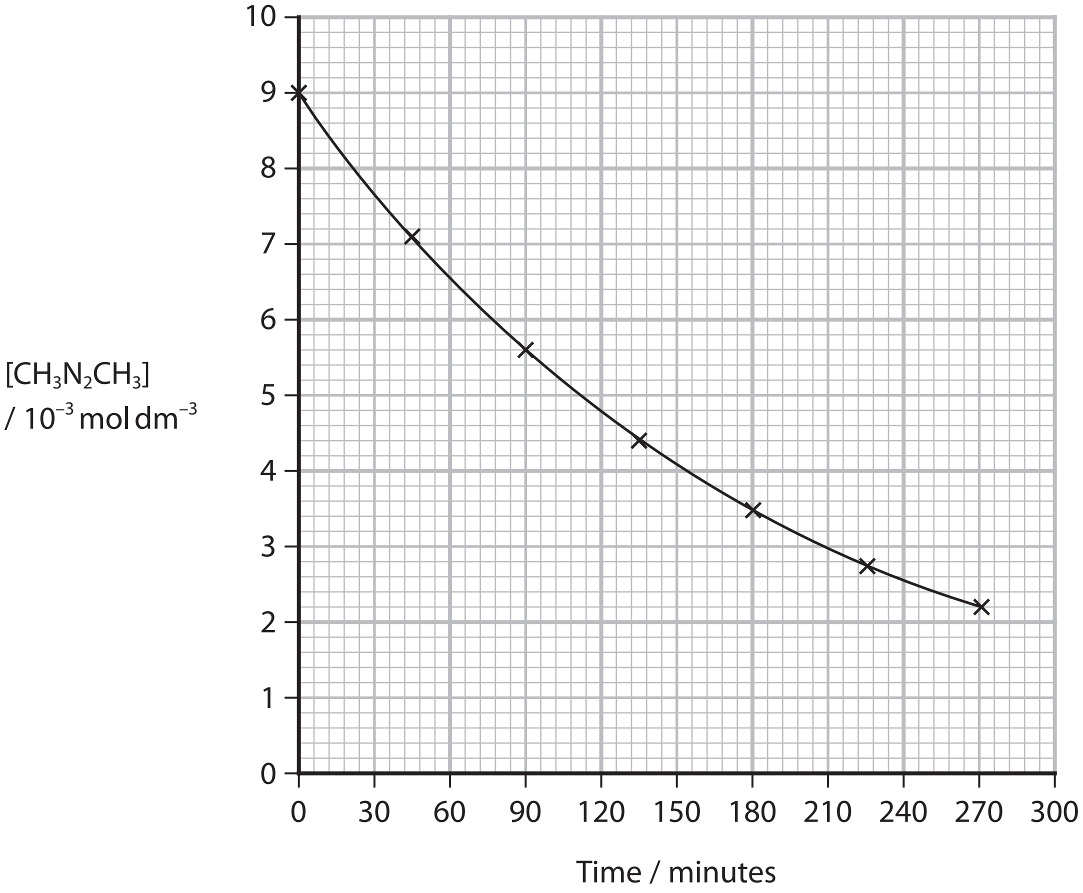
$$CH_3N_2CH_3(g) \rightarrow N_2(g) + C_2H_6(g)$$

(a) Write the rate equation for this first order reaction.

(1)

(b) The concentration of azomethane, $[CH_3N_2CH_3]$, was measured at various times during its decomposition at 573 K.

A graph of the data obtained is shown.



(i) Determine values for the half-life, $t_{1/2}$, of the decomposition of azomethane from the graph, stating whether or not these data confirm that the reaction is first order.
You must show your working on the graph.

(2)

(ii) Calculate the rate constant, k, **in s^{-1}**, for the decomposition of azomethane at 573 K, using your answer to (b)(i) and the expression shown.

$$t_{1/2} = \frac{\ln 2}{k}$$

(2)

(c) The rate constant for the decomposition of azomethane is $1.1 \times 10^{-6}\,\text{s}^{-1}$ at 523 K and $3.5 \times 10^{-3}\,\text{s}^{-1}$ at 623 K.

(i) Explain why the rate constant for this reaction is higher at 623 K than at 523 K.

(2)

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(ii) The rate constant changes with temperature according to the expression shown.

$$\log_{10}\left(\frac{k_1}{k_2}\right) = -\frac{E_a}{2.3R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Calculate the activation energy, E_a, for the decomposition of azomethane using this expression and the values for k at 523 K and 623 K.

Include units and give your answer to **two** significant figures.

[$R = 8.31\,\text{J mol}^{-1}\,\text{K}^{-1}$]

(3)

SECTION C

Answer ALL the questions. Write your answers in the spaces provided.

18 This question is about the homogeneous system

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

(a) Write the expression for the equilibrium constant, K_c, of this system.

(1)

(b) Chemist **A** carried out an experiment to determine K_c.

0.00500 mol of H_2 and 0.0100 mol of I_2 were heated in a sealed container of volume 1.00 dm^3.
At equilibrium, the mixture was found to contain 0.00968 mol of HI.

Calculate K_c, using these data and your expression from (a).
Include units, if any.
Give your answer to an appropriate number of significant figures.

(4)

(c) Chemist **B** determined the value of K_c at five different temperatures.

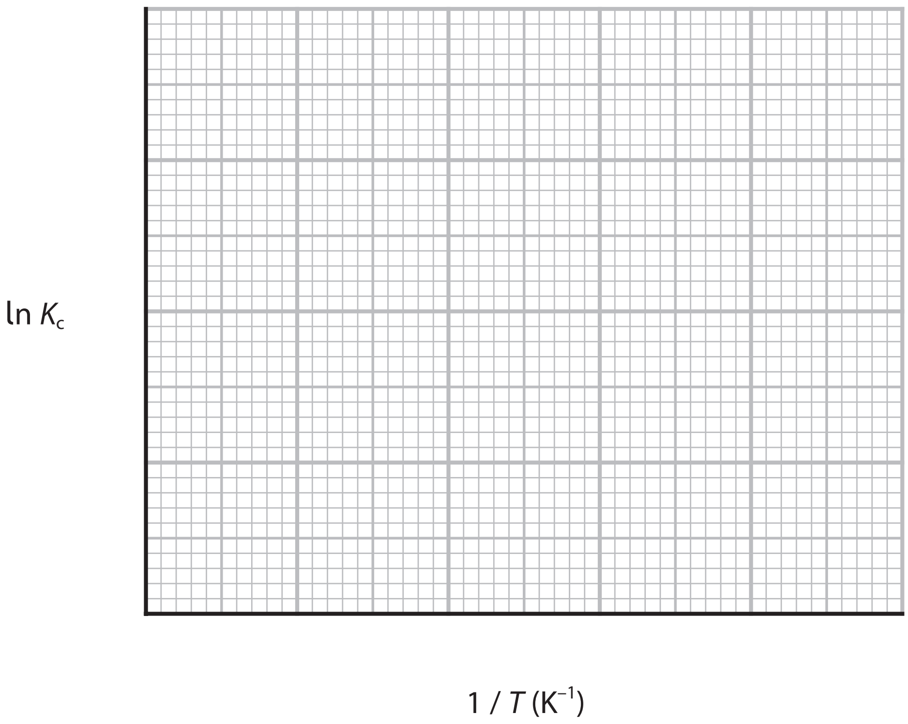
Temperature, T / K	$1/T$ (K^{-1})	K_c	ln K_c
523		122	4.80
577	0.00173	99.2	
620	0.00161	86.5	4.46
669	0.00149	75.6	4.33
721	0.00139	66.8	4.20

(i) Complete the table of data.

(2)

(ii) Plot a graph of ln K_c against $1/T$.
Include a line of best fit.

(3)



(iii) Determine the gradient of your graph.
You **must** show your working on the graph.

(1)

(iv) The gradient of the graph from (c)(iii) is related to the enthalpy change of the reaction, ΔH.

$$\text{gradient} = -\frac{\Delta H}{R}$$

Calculate ΔH, in J mol^{-1}, using your value for the gradient.

(2)

(v) The free energy change for the reaction, ΔG, is related to entropy and can be calculated from K_c.

$$\Delta G = -RT \ln K_c$$

Calculate ΔG at **620 K**, using this equation and data from the table. Include units.

(2)

(vi) The equation relating ΔG, ΔH and ΔS_{system} is shown.

$$\Delta G = \Delta H - T\Delta S_{\text{system}}$$

Calculate ΔS_{system} at 620 K, using your answers to (c)(iv) and (c)(v).

(2)

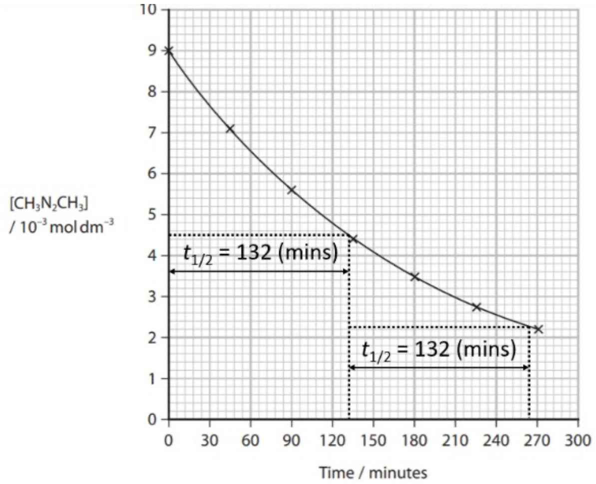
(d) Explain, in terms of the total entropy change, ΔS_{total}, why this reaction is feasible at any temperature.
Assume that both ΔH and ΔS_{system} are independent of temperature.

(3)

(Total for Question 18 = 20 marks)

TOTAL FOR SECTION C = 20 MARKS
TOTAL FOR PAPER = 90 MARKS

Question Number	Answer	Additional Guidance	Mark
16(a)	An answer that makes reference to the following points: • (rate =) $k[CH_3N_2CH_3]$	Accept rate = k[azomethane] Ignore state symbols even if incorrect Do not award non-square brackets	**1**

Question Number	Answer	Additional Guidance	Mark
16(b)(i)	An answer that makes reference to the following points:	Example of working on graph:  	**2**
	• determination of one half-life (with some working shown on graph) **(1)**	Allow half-life value between 126 and 138 Ignore units even if incorrect	
	• second half-life (with some working shown on graph) **and** constant (half-life shows reaction is first order) **(1)**	Allow half-life value between 126 and 138 Ignore units even if incorrect Allow similar for constant	

Question Number	Answer	Additional Guidance	Mark
16(b)(ii)	An answer that makes reference to the following points:	Example of calculation:	**2**
	- $t_{1/2}$ expression rearranged for k **(1)**	$k = \frac{\ln 2}{t_{1/2}}$	
	- calculation of k in s^{-1} **(1)**	$k = \frac{0.69315}{(132 \times 60)} = 8.7519 \times 10^{-5}$ / 0.000087519 (s^{-1}) TE on (b)(i) Ignore SF except 1SF Do not award 0.0052511 (s^{-1} / min^{-1}) Correct answer with some working scores (2)	

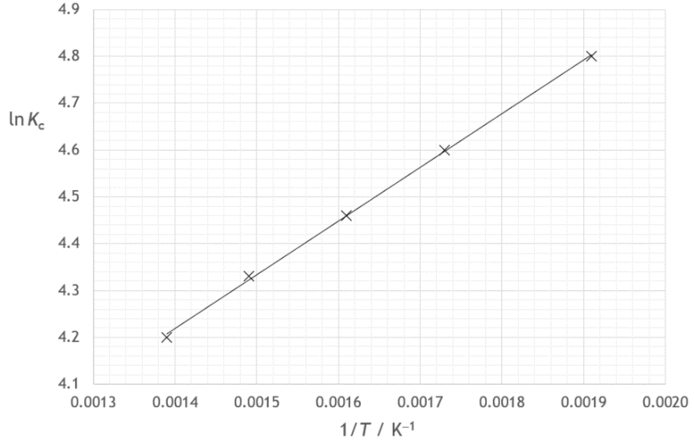
Question Number	Answer	Additional Guidance	Mark
16(c)(i)	An answer that makes reference to the following points:	Accept reverse arguments in M1 and M2	**2**
	- at a higher temperature more particles/collisions have ($E \geq$) E_a **(1)**	Ignore reference to successful collisions Ignore just particles/collision have more energy Ignore reference to collision frequency	
	- (therefore the) rate (of reaction) is higher **(1)**	**M2 is standalone mark** Allow (therefore the) half-life decreases	

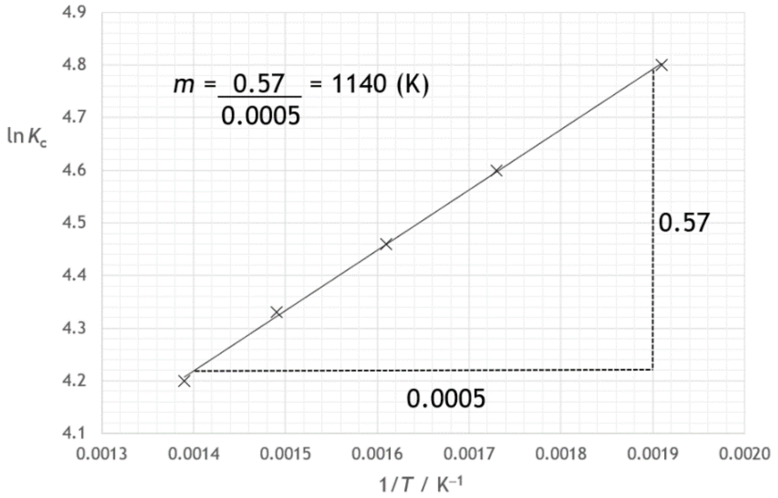
Question Number	Answer	Additional Guidance	Mark
16(c)(ii)	An answer that makes reference to the following points:	Example of calculation:	**3**
	- substitution of *k* and *T* values into expression **(1)**	$\log\left[\frac{1.1\times10^{-6}}{3.5\times10^{-3}}\right] = -\frac{E_a}{2.3\,R}\left[\frac{1}{523}-\frac{1}{623}\right]$ **or** $\log\left[\frac{3.5\times10^{-3}}{1.1\times10^{-6}}\right] = -\frac{E_a}{2.3\,R}\left[\frac{1}{623}-\frac{1}{523}\right]$	
	- calculation of E_a **(1)**	E_a = 218 130 (J mol^{-1}) / 218.13 (kJ mol^{-1}) Ignore sign Ignore units Ignore SF except 1SF TE on transposition of *k* and *T* values	
	- units of J mol^{-1} or kJ mol^{-1} **and** calculated answer to 2SF **(1)**	E_a = (+)220 000 J mol^{-1} / (+)220 kJ mol^{-1}	
		Correct answer with some working scores (3)	

Question Number	Answer	Additional Guidance	Mark
18(a)	An answer that makes reference to the following point: - correct expression	Example of correct expression: $(K_c =) \dfrac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$ Allow omission of state symbols Ignore any reference to units, even if incorrect Do not award non-square brackets	**1**

Question Number	Answer	Additional Guidance	Mark
18(b)	An answer that makes reference to the following points:	Correct answer with some working scores (4) Example of calculation:	**4**
	- moles H_2 and I_2 reacting **(1)**	$\dfrac{9.68 \times 10^{-3}}{2} = 4.84 \times 10^{-3}$ (mol)	
	- equilibrium moles H_2 **and** equilibrium moles I_2 **(1)**	$n(H_2) = 5.00 \times 10^{-3} - 4.84 \times 10^{-3} = 1.6 \times 10^{-4}$ (mol) $n(I_2) = 1.00 \times 10^{-2} - 4.84 \times 10^{-3} = 5.16 \times 10^{-3}$ (mol) TE on moles reacting provided +ve moles	
	- calculation of K_c **(1)**	(Because volume is 1 dm^3, mol = concentration) $(K_c =) \dfrac{(9.68 \times 10^{-3})^2}{(1.6 \times 10^{-4} \times 5.16 \times 10^{-3})} = 113.496$ TE on equilibrium moles TE on K_c expression from (a) for inverted expression or use of [HI] for $[HI]^2$ only Do not award −ve K_c value	
	- calculated answer to 3SF or 2SF **and** no units **(1)**	$(K_c =)$ 113 / 110 **and** no units Allow 114 **and** no units if 9.7×10^{-3} moles reacting TE on M3 TE on units from any K_c expression in (a)	

Question Number	Answer		Additional Guidance	Mark
18(c)(i)	An answer that makes reference to the following points:		**Penalise SF once only**	**2**
	• 1/*T* value to 3SF	**(1)**	0.00191 Accept 1.91×10^{-3} Calculator value is 0.001912045889	
	• ln K_c value to 3SF	**(1)**	4.60 Calculator value is 4.5971138014	

Question Number	Answer		Additional Guidance	Mark
18(c)(ii)	An answer that makes reference to the following points:		Example of graph:  	**3**
	• linear scales	**(1)**	points plotted must cover at least half of grid in each direction	
	• five points correctly plotted	**(1)**	Allow accuracy to ± half a small square	
	• straight line of best fit covering all points	**(1)**	Ignore extrapolations of line of best fit	

Question Number	Answer	Additional Guidance	Mark
18(c)(iii)	An answer that makes reference to the following point: • calculation of gradient (with some working)	Example of working on graph:  gradient = (+)1140 (K) Allow any value between 1060 and 1220 Allow use of data from the table provided points used lie on line of best fit Ignore units even if incorrect Ignore SF except 1 SF	**1**

Question Number	Answer	Additional Guidance	Mark
18(c)(iv)	An answer that makes reference to the following points: • rearrangement of expression for Δ*H* **(1)** • calculation of Δ*H* **(1)**	Example of calculation: Δ*H* = – gradient × *R* Δ*H* = –1140 × 8.31 = –9473.4 (J mol^{-1}) Accept –9.4734 kJ mol^{-1} Accept use of 8.314 for *R* TE on value of gradient from (c)(iii) Ignore SF except 1SF Do not award incorrect units	**2**

Question Number	Answer	Additional Guidance	Mark
18(c)(v)	An answer that makes reference to the following points: - calculation of ΔG **(1)** - units of ΔG **(1)**	Example of calculation: $\Delta G = -RT \ln K_c$ $= -8.31 \times 620 \times 4.46$ $= -22979$ (J mol^{-1})/-22.979 (kJ mol^{-1}) Accept −22980/−22.980 from use of ln(86.5) for 4.46 Accept use of 8.314 for R Ignore SF except 1SF Do not award omission of –ve sign **M2 dependent on use of $R \times T$ in M1** J mol^{-1} (from 8.31 × 620) OR kJ mol^{-1} (from 8.31/1000 × 620) Calculation of ΔG at any other temperature with correct units scores (1)	**2**

Question Number	Answer	Additional Guidance	Mark
18(c)(vi)	An answer that makes reference to the following points: • rearrangement of expression for ΔS_{system} **(1)** • calculation of ΔS_{system} **(1)**	Example of calculation: $\Delta S_{\text{system}} = \dfrac{(\Delta H - \Delta G)}{T}$ $\Delta S_{\text{system}} = \dfrac{(-9473.4 - (-22979))}{620}$ $= (+)21.783$ (J mol^{-1} K^{-1}, units can be in any order) Accept 0.021783 (kJ mol^{-1} K^{-1}, units can be in any order) TE on ΔH from (c)(iv) and ΔG from (c)(v) Ignore SF except 1SF Do not award incorrect units Correct answer scores (2)	**2**

Question Number	Answer	Additional Guidance	Mark
18(d)	An answer that makes reference to the following points: - $\Delta S_{\text{surroundings}}$ is (always) positive **and** (as) ΔH is negative **(1)**	Allow (as) reaction is exothermic Allow $\Delta S_{\text{surroundings}}$ is (always) negative **and** (as) ΔH is positive / reaction is endothermic as TE on (c)(iv)	**3**
	- ΔS_{system} is positive **(1)**	Allow $T\Delta S$ is positive Allow ΔS_{system} / $T\Delta S$ is negative as TE on (c)(vi)	
	- (so) ΔS_{total} is (always) positive **(1)**	**M3 dependent on positive $\Delta S_{\text{surroundings}}$ and positive ΔS_{system}** Accept (so) $\Delta S_{\text{total}} > 0$	

Total for Question 18 = 20 marks

Total for Section C = 20 marks

Total for Paper = 90 marks

SECTION B

Answer ALL the questions. Write your answers in the spaces provided.

17 The reaction between hydrogen peroxide and iodide ions in acid conditions is known as the Harcourt–Esson reaction after the scientists who first studied its kinetics.

$$H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow 2H_2O(l) + I_2(aq)$$

(a) A student carried out experiments to determine the rate equation for this reaction at 293 K.

(i) The rate of this reaction may be obtained by adding a fixed volume of sodium thiosulfate solution and a few drops of starch solution to the reaction mixture.

Explain how this method gives the rate of reaction.

(3)

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(ii) The student's results are shown.

Run	[H_2O_2(aq)] / mol dm^{-3}	[I^-(aq)] / mol dm^{-3}	[H^+(aq)] / mol dm^{-3}	Rate / mol dm^{-3} s^{-1}
1	0.0210	0.0198	0.00105	0.00181
2	0.0105	0.0400	0.00105	0.00181
3	0.0105	0.0797	0.00099	0.00364
4	0.0210	0.0801	0.00201	0.00730

Deduce the rate equation for this reaction.

(3)

(iii) Calculate the rate constant for this reaction at 293 K, using the results from Run 1. Include units with your answer.

(3)

(b) The student carried out a second series of experiments with this reaction at 313 K. The rate of reaction was found to be 4.45 times faster at 313 K than at 293 K.

Calculate the activation energy, E_a, for this reaction, using the Arrhenius equation. Give your answer to an appropriate number of significant figures and include units.

$$\ln k = -\frac{E_a}{RT} + \text{constant}$$

(4)

(Total for Question 17 = 13 marks)

20 Cracking reactions are used to obtain more useful compounds from the alkanes found in crude oil. An equation for the cracking of butane is shown.

$$C_4H_{10}(g) \rightarrow C_2H_6(g) + C_2H_4(g)$$

Thermodynamic data for the compounds in this reaction are given in the table.

	$C_4H_{10}(g)$	$C_2H_6(g)$	$C_2H_4(g)$
Standard molar entropy $S^\ominus$ / J K^{-1} mol^{-1}	310.1	229.5	219.5
Standard molar enthalpy change of formation $\Delta_f H^\ominus$ / kJ mol^{-1}	–126.5	–84.7	+52.2

(a) (i) Calculate the entropy change in the system, $\Delta S^\ominus_{system}$, for the cracking of butane.
Include a sign and units with your answer.

(2)

(ii) Calculate the enthalpy change of reaction, $\Delta_r H^\ominus$, for the cracking of butane.
Include a sign and units with your answer.

(2)

(iii) Calculate the entropy change in the surroundings, $\Delta S^{\ominus}_{\text{surroundings}}$, at 298 K for the cracking of butane, using your answer to (a)(ii).
Include a sign and units with your answer.

(2)

(iv) Calculate the total entropy change, $\Delta S^{\ominus}_{\text{total}}$, at 298 K for the cracking of butane, using your answers to (a)(i) and (a)(iii).
Include a sign and units with your answer.

(1)

(v) Calculate the temperature at which the cracking reaction becomes feasible.

(2)

(b) 5 mol of butane is cracked at 750 K. At equilibrium, 4.45 mol of ethene is formed and the total pressure is 1.20 atm.

$$C_4H_{10}(g) \rightleftharpoons C_2H_6(g) + C_2H_4(g)$$

(i) Give the expression for the equilibrium constant, K_p, for this reaction.

(1)

(ii) Calculate the value of K_p, including units if required.

(5)

(Total for Question 20 = 15 marks)

TOTAL FOR SECTION B = 51 MARKS

Section B

Question number	Answer	Additional guidance	Mark
17(a)(i)	An answer that makes reference to the following • sodium thiosulfate reacts with the iodine formed (1) • when (all) the sodium thiosulfate is used up has reacted the iodine reacts with the starch giving a blue-black colour (1) • the reciprocal of the time taken for the blue-black colour to appear is a measure of the rate (1)	Accept equation $S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$ Allow a blue-black colour forms at the end of the reaction Allow iodine reacts with the starch giving a blue-black colour Allow blue or black for blue-black Ignore reference to the colour of the solution before the starch-iodine complex forms Do not award iodide reacts with starch Allow 1/t = rate of reaction / 1/t $\propto$ rate of reaction Allow [reactant]/t $\propto$ rate of reaction Do not award thiosulfate as a reactant Allow (for M3) repeat experiment varying concentration of a reactant; plot concentration against time (for blue-black colour to appear) and measure **initial** gradient Ignore references to colorimeter	**(3)**

Question number	Answer	Additional guidance	Mark
17(a)(ii)	An answer that makes reference to the following		**(3)**
	- correct form of the rate equation (1)	Rate = $k[H_2O_2(aq)]^a[I^-(aq)]^b[H^+(aq)]^c$ or Rate = $k[H_2O_2(aq)]^a[I^-(aq)]^b$ Allow any values of a, b and c for M1 provided at least one value >0. Zero order species do not need to be shown Allow K for *k*	
	- values of three powers (including $[H^+]$ not shown) (2)	Rate = $k[H_2O_2(aq)][I^-(aq)][H^+(aq)]^0$ Accept Rate = $k[H_2O_2(aq)][I^-(aq)]$ For M2 deduct a mark for each incorrect power (reactant not shown order = 0) **Overall** mark for some of these responses including M1: Rate = $k[H_2O_2(aq)][I^-(aq)][H^+(aq)]$ scores (2) Rate = $k[H_2O_2(aq)]$ scores (2) Rate = $k[I^-(aq)]$ scores (2) Rate = $k[H_2O_2(aq)]^2[I^-(aq)]$ scores (2) Rate = $k[H_2O_2(aq)][H^+(aq)]$ scores (1) Rate = $k[I^-(aq)][H^+(aq)]$ scores (1) Ignore state symbols even if incorrect Correct answer with no intermediate stages scores (3) Use of round brackets deduct 1 mark	

Question number	**Answer**	**Additional guidance**	**Mark**
17(a)(iii)		Example of calculation TE on (a)(ii) for equations in correct form. Units must match the equation used	**(3)**
	• rearrangement of rate equation (1)	k = rate /([H_2O_2(aq)][I^-(aq)]) ignore state symbols	
	• calculation of value from Run 1 data (1)	$k = \frac{0.00181}{0.0210 \text{ x } 0.0198} = 4.3531$ Allow use of data from any run	
	• units of k (1)	$dm^3\ mol^{-1}\ s^{-1}$ Allow units in any order Allow mol^- for mol^{-1} here and throughout paper Ignore SF except 1 SF $k[I^-(aq)][H^+]$ gives 87.06 $dm^3\ mol^{-1}\ s^{-1}$ scores (3) if TE on (a)(ii) Correct answer with units but no working scores (3)	

Question number	**Answer**	**Additional guidance**	**Mark**
17(b)		Example of calculation	**(4)**
	• substitution of values for both temperatures into the Arrhenius equation (1)	ln k_{293} = constant $-\frac{E_a}{293\ xR}$ and ln k_{313} = constant $-\frac{E_a}{313\ xR}$	
	• subtraction and rearrangement of the two equations (1)	$\ln(\frac{k_{313}}{k_{293}}) = \ln 4.45 = \frac{E_a}{R}(\frac{1}{293}-\frac{1}{313})$	
	• solving equation to give value for E_a (1)	E_a = (+)56887	
	• answer to 2/3 SF **and** correct units (1)	(+)57000 / (+)56900 J mol^{-1} Or (+)57 / (+)56.9 kJ mol^{-1}	
		Correct answer with some working scores (4)	
		Some attempt at a calculation using the Arrhenius equation, giving a positive value to 2 or 3 SF and correct units scores M4	

(Total for Question 17 = 13 marks)

Question number	**Answer**	**Additional guidance**	**Mark**
20(a)(i)	• substitution of values into $\Delta S^{\circ}_{\text{system}} = S_{\text{products}} - S_{\text{reactants}}$ (1) • calculation of value from correct equation **and** sign and units (1)	In parts (i), (ii), (iii) and (iv) penalise omission of or incorrect units once only Allow units in any order Allow (e.g.) J/K/mol Do not award J/K mol Positive signs are not required Ignore SF except 1 SF throughout (a). Example of calculation $\Delta S^{\circ}_{\text{system}} = 229.5 + 219.5 - 310.1$ $= (+)138.9 \text{ J K}^{-1} \text{ mol}^{-1}$ TE for transcription errors on values only Correct answer with no working scores (2)	**(2)**

Question number	**Answer**	**Additional guidance**	**Mark**
20(a)(ii)	• substitution of values into $\Delta_r H^{\circ} = \Delta_f H^{\ominus}(\text{products}) - \Delta_f H^{\ominus}(\text{reactants})$ (1) • calculation of value from correct equation **and** sign and units (1)	Example of calculation $\Delta_r H^{\circ} = (-84.7 + 52.2) - (-126.5)$ $= (+)94.0 \text{ kJ mol}^{-1}$ Correct answer with no working scores (2) TE for transcription errors on values $-94.0 \text{ kJ mol}^{-1}$ scores (1) $-159.0 \text{ kJ mol}^{-1}$ scores (1) $(+)263.4 \text{ kJ mol}^{-1}$ scores (1) $-10.4 \text{ kJ mol}^{-1}$ scores (1)	**(2)**

Question number	Answer	Additional guidance	Mark
20(a)(iii)	• equation for $\Delta S^{o}_{surroundings}$ **and** substitution of values (1) • calculation of value from correct equation **and** sign and units (1)	Example of calculation $\Delta S^{o}_{surroundings} = -\Delta H / T$ $= -94000 \div 298$ Accept $= -94 \div 298$ $= -315.44\ J\ K^{-1}\ mol^{-1} / -0.31544\ kJ\ K^{-1}\ mol^{-1}$ TE on $\Delta_r H^{o}$ from (a)(ii) Do not award use of incorrect equation Correct answer with no working scores (2)	**(2)**

Question number	Answer	Additional guidance	Mark
20(a)(iv)	• equation for ΔS^{o}_{total} **and** substitution of values **and** calculated value with sign and units	Example of calculation $\Delta S^{o}_{total} = \Delta S^{o}_{system} + \Delta S^{o}_{surroundings}$ $= +138.9 + -315.44$ $= -176.54\ J\ K^{-1}\ mol^{-1}$ Accept $= +0.1389 + -0.31544$ $= -0.17654\ kJ\ K^{-1}\ mol^{-1}$ TE on valuesfrom (a)(i) and (a)(iii) Do not award use of incorrect equation Do not award value obtained using mixed units Correct answer with no working scores (1)	**(1)**

Question number	Answer	Additional guidance	Mark
20(a)(v)	- equation for feasibility (1) substitution of values **and** evaluation of T (1)	Example of calculation $(\Delta S^{o}_{\text{system}} + (-\Delta H/T) = \Delta S^{o}_{\text{total}} = 0)$ $\Delta S^{o}_{\text{system}} = \Delta H/T$ or $-\Delta S^{o}_{\text{system}} = -\Delta H/T$ $T = 94000 \div 138.9$ = 676.746 (K) (from unrounded values) Accept 403.746(°C) TE on valuesfrom (a)(i) and (a)(ii) Do not award use of incorrect equation (e.g. omission of negative sign in $\Delta S^{o}_{\text{surroundings}}$ expression) Do not award value obtained using mixed units Correct answer with no working scores (2)	**(2)**

Question number	Answer	Additional guidance	Mark
20(b)(i)	- equilibrium constant expression	Example of expression $K_p = \dfrac{p(C_2H_6) \text{ x } p(C_2H_4)}{p(C_4H_{10})}$ Accept p_x where x = formula or pp(X) Ignore state symbols even if incorrect Do not award square brackets	**(1)**

<table>
<tr><th>Question number</th><th>Answer</th><th>Additional guidance</th><th>Mark</th></tr>
<tr>
<td>20(b)(ii)</td>
<td>
• moles of reactants and products (1)
• mole fractions (1)
• partial pressures (1)
• substitution of values into K_p equation and evaluation (1)
• units (1)
</td>
<td>
Example of calculation
<table>
<tr><th></th><th>C_4H_{10}</th><th>C_2H_6</th><th>C_2H_4</th></tr>
<tr><td>mol at equil^m</td><td>5 – 4.45
= 0.55</td><td>4.45</td><td>4.45</td></tr>
<tr><td>mole fraction</td><td>$\frac{0.55}{9.45}$
= 0.05820</td><td>$\frac{4.45}{9.45}$
= 0.47090</td><td>$\frac{4.45}{9.45}$
= 0.47090</td></tr>
<tr><td>partial pressures</td><td>1.20 x 0.05820
= 0.06984</td><td>1.20 x 0.47090
= 0.56508</td><td>1.20 x 0.47090
= 0.56508</td></tr>
</table>
$K_p = \frac{0.56508^2}{0.069841} = 4.5721$ (4.5720 with unrounded numbers)
= (4.5721) atm
Ignore SF except 1 SF
TE on expression in (b)(i) that contains at least two species
TE at each stage
Correct answer with units but no working scores (5)

Omission of partial pressure gives K_p = 3.8100 atm scores (4)
Omission of mole fraction gives K_p = 43.21 atm scores (4)
</td>
<td>(5)</td>
</tr>
</table>

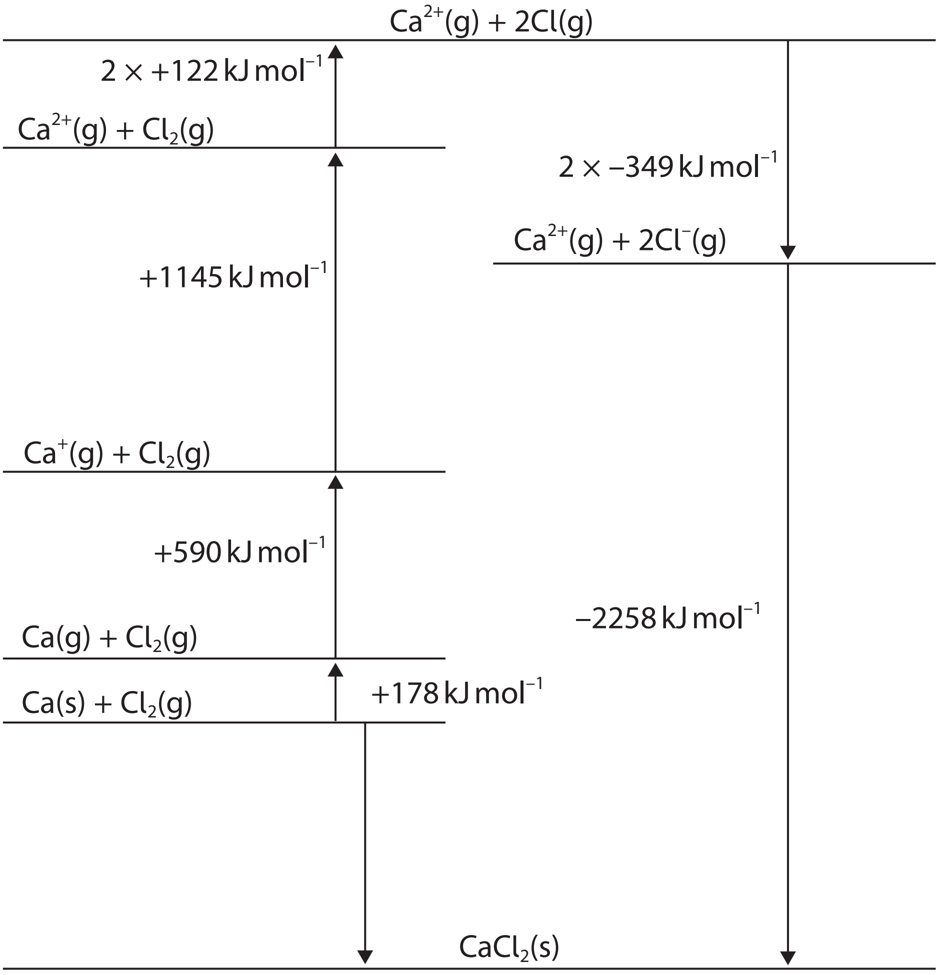
(Total for Question 20 = 15 marks)

TOTAL FOR SECTION B = 51 MARKS

SECTION B

Answer ALL the questions. Write your answers in the spaces provided.

17 A Born–Haber cycle for calcium chloride is shown.



(a) State the value of the $\Delta_{at}H$ for calcium.

(1)

....

(b) Calculate the enthalpy change of formation for calcium chloride.

(2)

(c) Some energy data are shown.

Compound	Theoretical lattice energy / kJ mol^{-1}	Experimental lattice energy / kJ mol^{-1}
$CaCl_2$	–2223	–2258
CaI_2	–1905	–2074

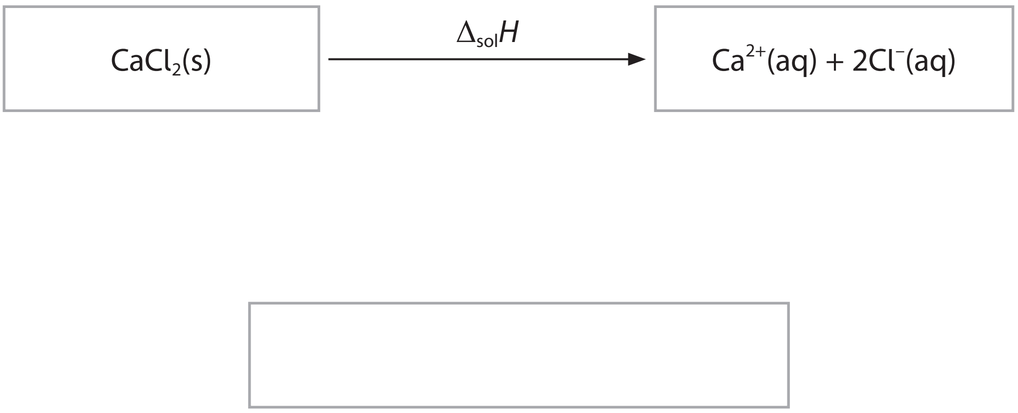
Explain why the difference between the theoretical and the experimental values for lattice energy is very much greater for calcium iodide than for calcium chloride.

(4)

(d) Calcium chloride is soluble in water.

(i) Complete the energy cycle including labelled arrows.

(2)



(ii) Calculate the enthalpy change of solution, $\Delta_{sol}H$, for calcium chloride using the data given and the completed energy cycle in (d)(i).

(2)

Data	Energy change / kJ mol^{-1}
LE ($CaCl_2(s)$)	–2258
$\Delta_{hyd}H$ ($Ca^{2+}(g)$)	–1579
$\Delta_{hyd}H$ ($Cl^-(g)$)	–378

(Total for Question 17 = 11 marks)

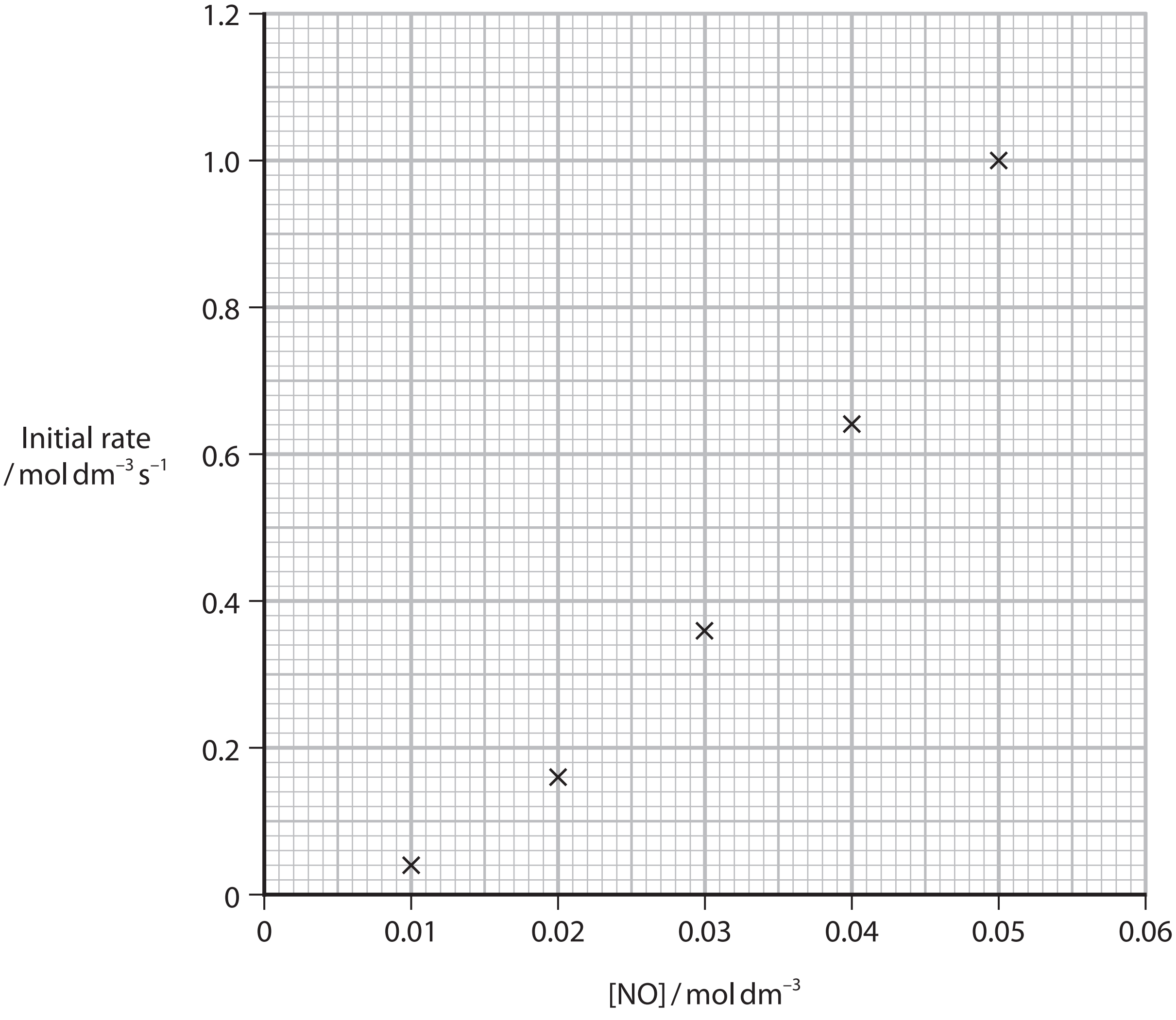
18 This question is about the reaction between nitrogen monoxide and oxygen.

$$NO(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO_2(g)$$

(a) The results of a series of kinetics experiments are shown.

Experiment	Initial [NO] / mol dm^{-3}	Initial [O_2] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.010	0.050	0.040
2	0.020	0.050	0.160
3	0.030	0.050	0.360
4	0.040	0.050	0.641
5	0.050	0.050	1.001
6	0.020	0.025	0.080

The data for experiments 1–5 were plotted on a graph.



(i) Draw a best-fit line on the graph.

(1)

(ii) State how the graph shows that the reaction is **not** first order with respect to nitrogen monoxide.

(1)

....

....

(iii) Deduce the orders of reaction with respect to NO and O_2, using the data from experiments 1–6.

(2)

Order with respect to NO = ...

Order with respect to O_2 = ...

(iv) Write the rate equation for the reaction, using your answer to (a)(iii).

(1)

(v) Calculate the rate constant for this reaction using the data from experiment 1 and your rate equation. Include units in your answer.

(2)

(b) The equilibrium constant, K_p, for the reaction at 298 K is 1.55×10^6 $\text{atm}^{-½}$.

State what this value of the equilibrium constant indicates about the position of the equilibrium. Justify your answer.

(2)

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(Total for Question 18 = 9 marks)

20 Nitrous oxide, N_2O, decomposes at high temperature to form nitrogen and oxygen.

$$N_2O(g) \rightleftharpoons N_2(g) + \tfrac{1}{2}O_2(g)$$

(a) (i) Some standard molecular entropy data are shown.

Substance	Standard molecular entropy $S^\ominus$ / $J\,K^{-1}\,mol^{-1}$
nitrogen, N_2	192
oxygen, O_2	205
nitrous oxide, N_2O	220

Calculate the standard entropy change of the system for the decomposition shown.
Include a sign and units in your answer.

(2)

(ii) The standard enthalpy change of the forward reaction is −82 kJ mol^{-1}.

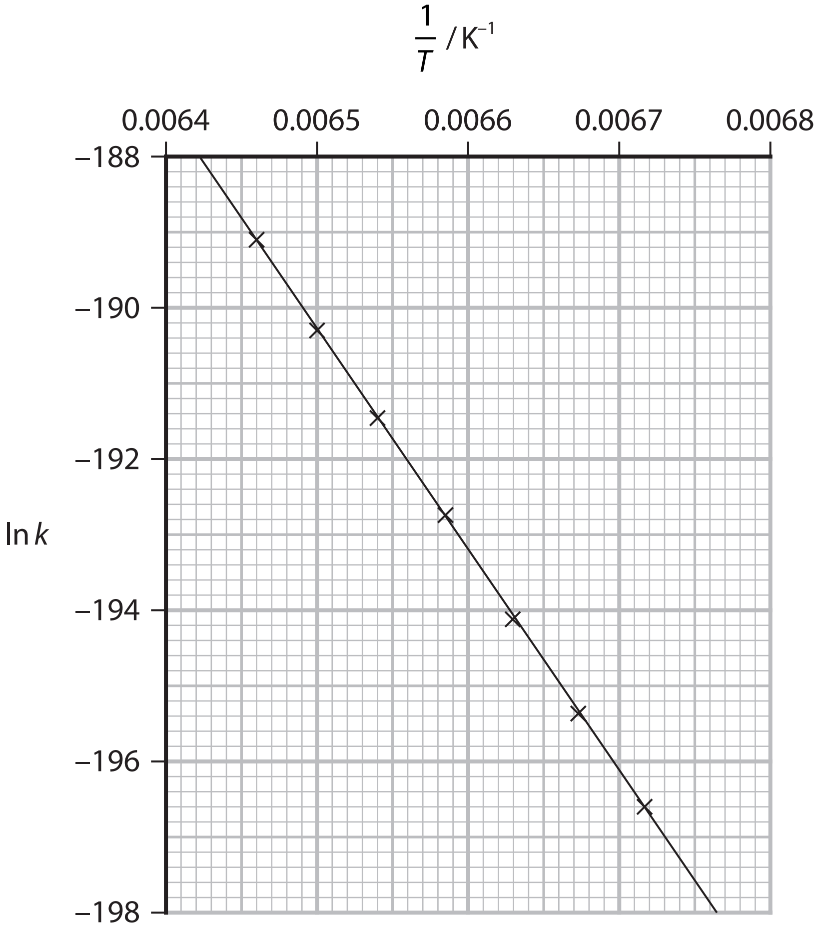
Calculate the entropy change of the surroundings at 2048 K.
Include a sign and units in your answer.

(2)

(iii) Calculate the total entropy change of the reaction at 2048 K.
Include a sign and units in your answer.

(1)

(b) Rate experiments on the decomposition of nitrous oxide produced the following graph.



Calculate the activation energy for the reaction in $kJ\,mol^{-1}$.
Include the value of the gradient.

$$\ln k = -\frac{E_a}{R}\frac{1}{T} + \text{constant}$$

$R = 8.31\ J\,K^{-1}\,mol^{-1}$

(2)

(c) Explain whether or not this reaction occurs at 2048 K by considering the values calculated in (a) and (b).

(2)

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....

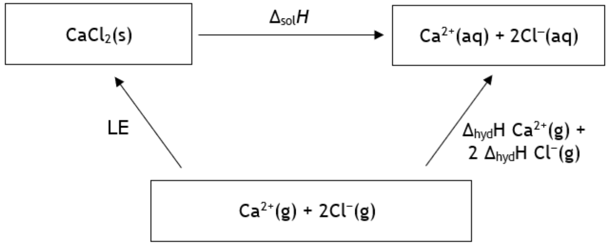
(Total for Question 20 = 9 marks)

Section B

Question Number	Answer	Additional Guidance	Mark
17(a)	• (+)178 (kJ mol^{-1})	Do not award –178 (kJ mol^{-1}) Ignore units even if incorrect	**(1)**

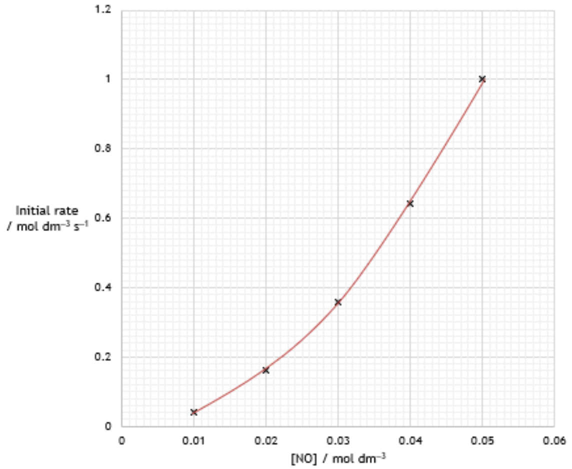
Question Number	Answer	Additional Guidance	Mark
17(b)	• equation or workings **(1)** • answer to 3SF with negative sign **(1)**	Example of calculation: $\Delta_f H = \Sigma$(all other terms) $\Delta_f H = 178 + 590 + 1145 + (2 \times 122) + (2 \times -349) + (-2258)$ –799 (kJ mol^{-1}) Correct answer scores (2) TE on incorrectly transferred values e.g. –394 Penalise omission of ×2 once only (–572 scores 1 mark) TE on one incorrect sign No TE on incorrect expression Penalise M2 for incorrect units +799 scores 1 mark	**(2)**

Question Number	Answer	Additional Guidance	Mark
17(c)	An explanation that makes reference to the following points:	Allow reverse arguments	**(4)**
	- calcium chloride is almost completely ionic **(1)**	Accept $CaCl_2$ is 100% ionic Allow LE is calculated assuming a pure ionic structure	
	- calcium iodide has partially covalent character **(1)**	Allow shows more covalent character Allow $CaCl_2$ has less covalent character than CaI_2 Ignore polar Do not award M2 for CaI_2 is covalent Do not award M2 for Intermolecular forces	
	- iodide (ion) is larger (than chloride (ion)) **(1)**	Accept iodide has a lower charge density Allow iodine ion Ignore iodine is larger Do not award molecules, Cl_2 or I_2 loses M3	
	- (so) more (easily) polarised **(1)**	Accept more (easily) distorted Allow (more) polarisable Do not award CaI_2 is more polarised If no comparison for M3 and M4 allow 1 mark, e.g., "iodide is large and is polarised" Penalise iodine/chlorine or incorrect ions once only.	

Question Number	Answer	Additional Guidance	Mark
17(d)(i)	An answer that makes reference to the following points: - two labelled arrows in the correct direction **(1)** - formulae including state symbols **(1)**	An example of a completed cycle:  Accept two arrows on right-hand side Allow $\Delta_{\text{latt}}H$/ ΔH_{latt} Allow $\Delta_{\text{hyd}}H$ alone on right-hand arrow Allow ΔH_{hyd} Allow numerical values rather than the symbols Allow missing 2 for the $\Delta_{\text{hyd}}H\ Cl^-$ Allow left arrow going down if labelled as lattice dissociation energy or –LE	**(2)**

Question Number	Answer	Additional Guidance	Mark
17(d)(ii)	- calculation **(1)** - enthalpy change of solution **(1)**	Example of a calculation: $-(-2258) - 1579 - (2 \times 378)$ $= -77$ (kJ mol^{-1}) No TE on an incorrect cycle, but (+)77 scores 1 mark Allow TE on transcription errors from M1, and award M2 Allow ×2 omitted, answer = (+)301 (kJ mol^{-1}) scores (1)	**(2)**

(Total for Question 17 = 11 marks)

Question Number	Answer	Additional Guidance	Mark
18(a)(i)	- smooth line of best-fit through all the points	An example of a graph:  Ignore extrapolation at either end of the best-fit line Allow non-smooth lines, within 1 square of each point Do not award use of a ruler	**(1)** **Expert**

Question Number	Answer	Additional Guidance	Mark
18(a)(ii)	- graph is not a straight line (through the origin)	Accept reverse argument Accept 1st order would be a straight line Accept the relationship is not linear / directly proportional Allow 2nd order with justification e.g., as it's a curve or rate quadruples when concentration doubles Ignore half lives Allow rate not doubling when concentration is doubled Ignore gradient not constant. Ignore exponential No TE 18(a)(i)	**(1)**

Question Number	Answer	Additional Guidance	Mark
18(a)(iii)	An answer that makes reference to the following points: • order of reaction for NO **(1)** • order of reaction for O_2 **(1)**	 2 / 2nd / second 1 / 1st / first	**(2)**

Question Number	Answer	Additional Guidance	Mark
18(a)(iv)	• rate = $k[NO]^2[O_2]$	Allow TE on incorrect orders in a(iii) Allow r on LHS Do not award round brackets Must be a rate equation to gain the mark Correct answer scores 1	**(1)**

Question Number	Answer	Additional Guidance	Mark
18(a)(v)	• substitution **or** rearrangement **(1)** • answer **and** units **(1)**	Example of a calculation: $0.040 = k\,(0.010)^2(0.05)$ $k = \frac{0.040}{(0.010)^2(0.05)}$ $= 8000\ dm^6\ mol^{-2}\ s^{-1}$ Allow units in any order Allow s^{-} Allow $dm^6/mol^2\ s$ but not $dm^6/mol^2/s$ Allow TE on a(iv) for both marks, units must match order for M2 Correct answer with units scores 2, even if expression in Q18(a)(iv) is incorrect	**(2)**

Question Number	Answer	Additional Guidance	Mark
18(b)	An answer that makes reference to the following points: • the equilibrium constant is (very) large **(1)** • the equilibrium position is (far) to the right / (heavily) favours the products **(1)**	Allow K_p >>1 Allow synonyms e.g., huge, massive, etc. Allow high Ignore quite large Ignore K_p >1, positive Ignore numerator is larger than the denominator Ignore references to partial pressures Allow goes to completion Do not award "shifts to the right" Ignore favours the forward reaction Do not award M2 for comments on rate For two marks there must be a comment on extent/magnitude	**(2)**

(Total for Question 18 = 9 marks)

Question Number	Answer	Additional Guidance	Mark
20(a)(i)	 • expression or suitable working **(1)** • correct answer **(1)**	Example of a calculation: (192 + 0.5 × 205) – (220) (+)74.5 (J K^{-1} mol^{-1}) Correct answer scores 2 –74.5 scores 0 TE on small errors in M1 e.g., miss out 0.5, as long as the answer is positive Penalise incorrect units once only for ai-aiii Allow J K^{-} mol^{-} Allow J/K mol but not J/K/mol	**(2)**

Question Number	Answer	Additional Guidance	Mark
20(a)(ii)	 • balanced equation or suitable working **(1)** • correct answer **(1)**	Example of a calculation: ΔS surroundings = $-\Delta H/T$ = – (–82000) ÷ (2048) = 82000 ÷ 2048 (+) 40.039 (J K^{-1} mol^{-1}) Correct answer scores 2 Ignore SF – 40 scores 1 mark 0.04 scores 1 mark with correct units or without units, 2 marks with kJ K^{-1} mol^{-1}	**(2)**

Question Number	Answer	Additional Guidance	Mark
20(a)(iii)	- total entropy change	Example of a calculation: 74.5 + 40.0 = (+)114.5 (J K^{-1} mol^{-1}) TE on ai and aii, but both must be in the correct units Ignore SF except 1SF	**(1)**

Question Number	Answer	Additional Guidance	Mark
20(b)	- gradient **(1)** - activation energy **(1)**	Example of a calculation: $\dfrac{(-197)-(-190)}{(0.00673)-(0.00649)} = \dfrac{-7}{0.00024}$ gradient = –29 167 (K) (allow any negative value between 28 300-30 000) (– 8.31 × – 29 167) ÷1000 = (+)242.4 (kJ mol^{-1}) (allow values between 235.1 to 249.3 for 2 marks) Ignore SF except 1 SF Allow TE from M1 Answers in J mol^{-1} score both marks if in the allowed range (235100-249300)	**(2)**

Question Number	Answer	Additional Guidance	Mark
20(c)	An explanation that makes reference to the following points: • (thermodynamically) feasible because ΔS_{total} is positive **(1)** • activation energy high so the reaction is very slow (at low temperatures) **(1)**	Ignore thermodynamically stable/unstable Allow high temperature will provide E_a so reaction will proceed Allow reaction may not happen as E_a is (very) high Allow high E_a so kinetically stable Allow high E_a so kinetically non-feasible TE on 20(a)(iii) but not on 20(b)	**(2)**

(Total for Question 20 = 9 marks)

3 This question is about an experiment to investigate the kinetics of the reaction between iodine and propanone with an acid catalyst.

The equation for the reaction is shown.

$$I_2(aq) + CH_3COCH_3(aq) + H^+(aq) \rightarrow CH_3COCH_2I(aq) + 2H^+(aq) + I^-(aq)$$

To obtain the order of reaction with respect to iodine, the concentration of iodine in the reaction mixture was determined at various times.

Procedure

Step **1** Mix 25 cm^3 of 1.0 mol dm^{-3} sulfuric acid with 25 cm^3 of 1.0 mol dm^{-3} propanone in a beaker.

Step **2** Start a clock as 50 cm^3 of 0.020 mol dm^{-3} iodine solution is added to the beaker. Mix the reactants thoroughly.

Step **3** Tip a spatula measure of sodium hydrogencarbonate into a conical flask. After 3 minutes, pipette a 10.0 cm^3 sample of the reaction mixture into the conical flask and mix thoroughly.

Step **4** Titrate the iodine in the sample with 0.010 mol dm^{-3} sodium thiosulfate solution using a suitable indicator. Record the titre.

Step **5** Repeat Steps **3** and **4** every 3 minutes to obtain four more titres.

(a) State why the sulfuric acid and propanone concentrations are both much larger than the iodine concentration.

(1)

....

....

(b) State why sodium hydrogencarbonate is used in Step **3**.

(1)

....

....

(c) Name the indicator that would be used for the titration in Step **4**, stating the colour **change** that would be seen at the end-point of the reaction.

(2)

....

....

(d) Titration results from the experiment are shown.

Time / minutes	3	6	9	12	15
Titre / cm^3	16.05	15.30	14.50	13.70	12.95

(i) Plot a graph of titre against time.

(3)

(ii) State why the volume of thiosulfate may be used for plotting the graph rather than the concentration of iodine.

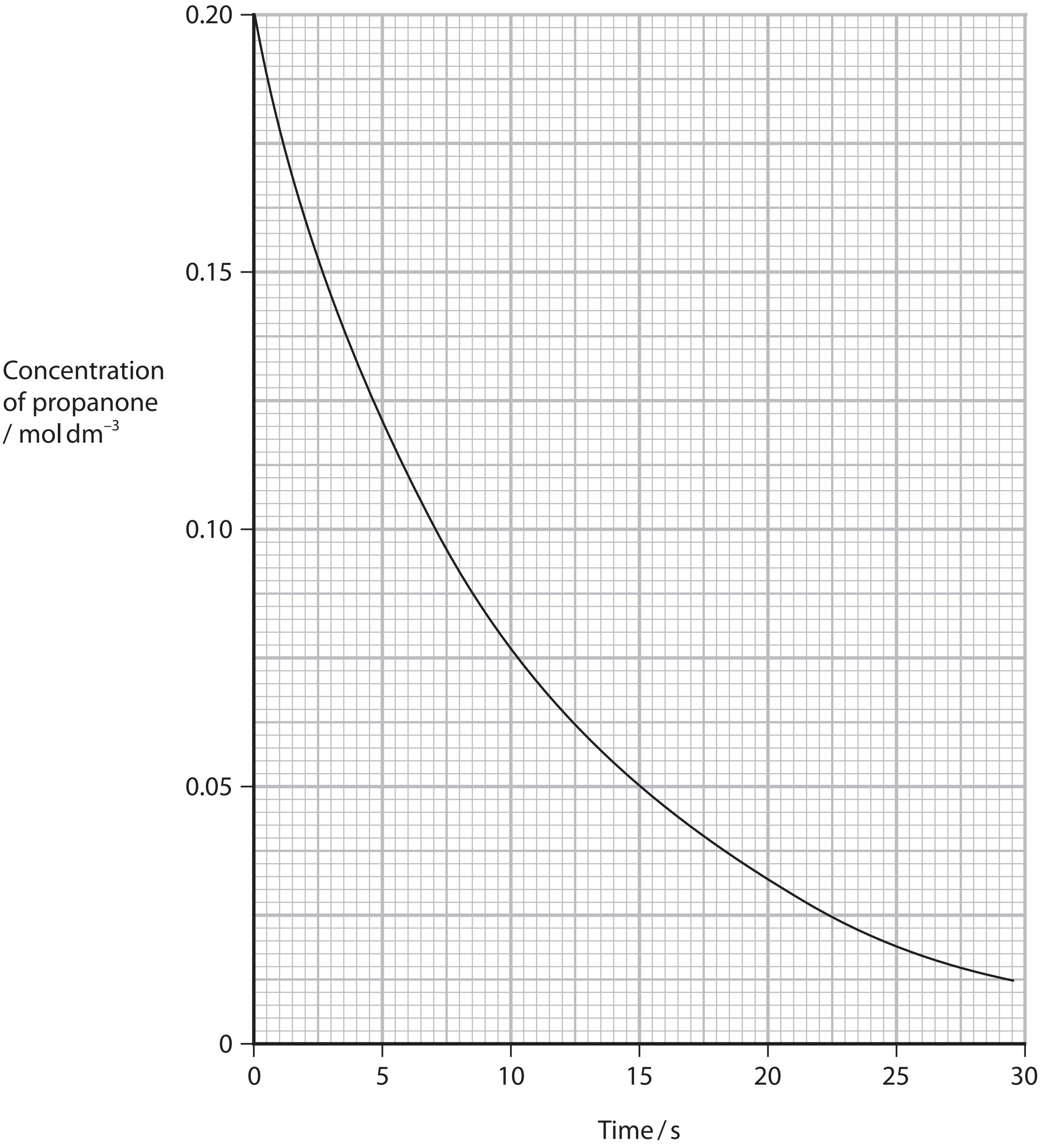
(1)

(iii) State the order of reaction with respect to iodine.
Justify your answer by referring to your graph.

(1)

(e) Further experiments were carried out to determine the reaction orders with respect to propanone and sulfuric acid.

(i) A graph of the concentration of propanone against time is shown.



The reaction is first order with respect to propanone.

Determine two half-lives for this reaction.
You **must** show your working on the graph.

(2)

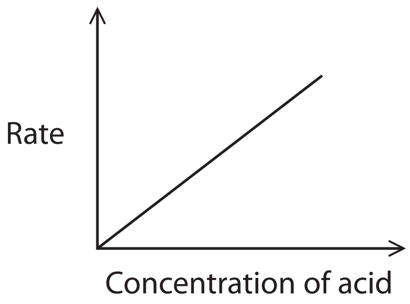
First half-life

....

Second half-life

....

(ii) A graph of the reaction rate against the concentration of sulfuric acid is shown.



Deduce the rate equation for the overall reaction of iodine and propanone with an acid catalyst.
Use your answer from (d)(iii) and information from (e)(i) and the graph in (e)(ii).

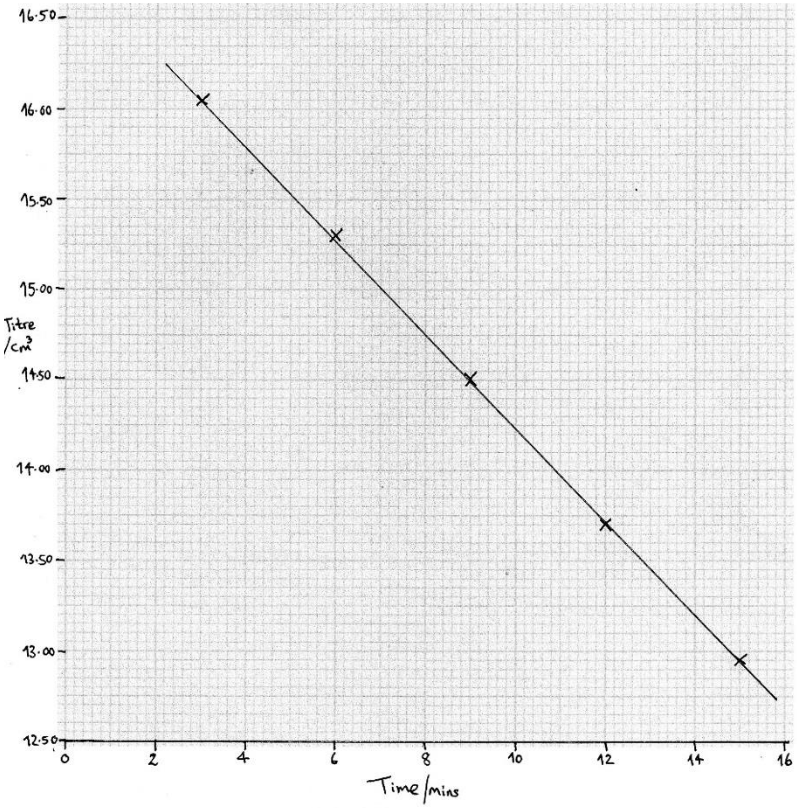
(1)

(Total for Question 3 = 12 marks)

Question Number	Answer	Additional Guidance	Mark
3(a)	An answer that makes reference to the following point: • only the iodine concentration affects the rate OR so the concentrations of sulfuric acid and propanone do not affect the rate	Allow so only the iodine concentration changes (significantly) Allow [H^+] and [CH_3COCH_3] do not change (significantly) / (effectively) zero order (wrt [H^+] and [CH_3COCH_3]) Ignore just concentrations of H_2SO_4 and CH_3COCH_3 are in excess Ignore comments on limiting reagents	(1)

Question Number	Answer	Additional Guidance	Mark
3(b)	An answer that makes reference to the following point: • to stop / quench the reaction	Allow neutralise/remove the (sulfuric) acid/H^+ (catalyst) Ignore slow the reaction Do not award to remove OH^-	(1)

Question Number	Answer	Additional Guidance	Mark
3(c)	An answer that makes reference to the following points: • (indicator) starch (solution) **(1)** • (colour change) blue-black/(dark)blue/black to colourless **(1)**	**M2 is dependent on M1** Ignore colour before addition of starch	(2)

Question Number	Answer	Additional Guidance	Mark
3(d)(i)		Example of graph:  	**(3)**
	• axes labelled correctly with units and suitable scale **(1)**	Points plotted must cover at least 50% of the graph in both directions	
	• all points plotted correctly **(1)**	Allow ±1 small square	
	• best fit **straight** line **(1)**	Ignore extrapolation	

Question Number	Answer	Additional Guidance	Mark
3(d)(ii)	An answer that makes reference to the following point: • the volume of (sodium) thiosulfate / titre is (directly) proportional to the concentration of iodine	Allow they are (directly) proportional Ignore any comments on correlation	**(1)**

Question Number	Answer	Additional Guidance	Mark
3(d)(iii)	An answer that makes reference to the following point: • zero (order) / 0 **and** straight line (with a negative gradient) graph	Accept rate is proportional to 1/time Accept changes to iodine concentration have no affect on rate Accept zero order **and** gradient is constant Ignore reference to sign of gradient NOTE: the order wrt iodine must be used in (e)(ii) COMMENT: allow linear for straight line	**(1)**

Question Number	Answer	Additional Guidance	Mark
3(e)(i)	An answer that makes reference to the following points: • working shown on graph for two half lives **(1)** • two half-lives of 7 and 8 (seconds) **(1)**	Allow a range of 6 – 9 (seconds) Ignore references to constant half life Do not award minutes / min	**(2)**

Question Number	Answer	Additional Guidance	Mark
3(e)(ii)	An answer that makes reference to the following point: • rate = k[CH_3COCH_3][H^+]	Allow r for rate Allow H_2SO_4 / acid for H^+ Allow names for formulae Accept inclusion of '1' for powers Allow TE from diii Ignore inclusion of $[I_2]^0$ NOTE: The order wrt to iodine must be consistent with the answer in 3(d)(iii) Ignore state symbols even if incorrect	**(1)**

(Total for Question 3 = 12 marks)

15 A reaction vessel contained nitrogen monoxide and oxygen in a 2 : 1 molar ratio.
The mixture was allowed to come to equilibrium forming nitrogen dioxide.
The equation for the reaction is shown.

$$2NO + O_2 \rightleftharpoons 2NO_2$$

The volume of the vessel was 15 dm^3 and the reaction was carried out at a constant temperature and at a pressure of 200 000 Pa.

At equilibrium there was a total of 0.69625 mol of gas in the reaction vessel and the mass of oxygen was 7.000 g.

(a) (i) Calculate the number of moles of each substance at equilibrium.

(3)

(ii) Calculate the value of K_c under these conditions.
Include units in your answer.

(4)

(b) Calculate the temperature, in K, of the reaction mixture at equilibrium under these conditions.
Use the equation $pV = nRT$ and the data at the start of the question.

(3)

(c) Under a different set of conditions, the reaction was carried out to find the initial rate of reaction.

Experiment number	Initial [NO] / mol dm^{-3}	Initial [O_2] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	6.50×10^{-2}	1.25×10^{-2}	6.87×10^{-4}

The rate equation for this reaction is

$$\text{rate} = k[\text{NO}]^2[\text{O}_2]$$

(i) Give the reason why colorimetry can be used to monitor the rate of the reaction.

(1)

(ii) Use the data from Experiment 1 to find the value of the rate constant, *k*. Include units in your answer.

(2)

(iii) State why the reaction is unlikely to proceed in a single step.

(1)

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(iv) A student proposed the mechanism shown for this reaction.

$$2NO \rightleftharpoons N_2O_2 \quad \text{slow}$$

$$N_2O_2 + O_2 \rightarrow 2NO_2 \quad \text{fast}$$

Justify whether or not this mechanism is consistent with the overall equation for the reaction **and** with the rate equation.

(2)

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(Total for Question 15 = 16 marks)

16 Iron, lead and zinc can be extracted using a blast furnace but aluminium cannot.

In a blast furnace, iron is extracted from iron(III) oxide, Fe_2O_3, at high temperature.

Some standard enthalpy changes of formation, $\Delta_f H^\ominus$, and standard molar entropies, $S^\ominus$, are shown.

Substance	Al(s)	Al_2O_3(s)	CO(g)	CO_2(g)	Fe(s)	Fe_2O_3(s)
$\Delta_f H^\ominus$ / kJ mol^{-1}	0	–1676	–111	–394	0	–824
$S^\ominus$ / J K^{-1} mol^{-1}	28.3	50.9	197.6	213.6	27.3	87.4

(a) The main reaction occurring in the blast furnace to form iron is shown.

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$$

This reaction is feasible at all temperatures.

(i) Calculate the standard entropy change of the system for this reaction.

(3)

(ii) Calculate the standard enthalpy change for this reaction.

(3)

(iii) Explain how your answers to (a)(i) and (a)(ii) show that this reaction is feasible at all temperatures.

(3)

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(b) The main reduction reaction of aluminium oxide in a blast furnace is shown.

$$Al_2O_3 + 3CO \rightarrow 2Al + 3CO_2$$

(i) Calculate the temperature at which this reaction becomes feasible.

(4)

(ii) Suggest why aluminium is not extracted from its oxide using a blast furnace.

(1)

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(Total for Question 16 = 14 marks)

Question Number	Answer	Additional Guidance	Mark
15(a)(i)	- calculation of moles of oxygen at equilibrium **(1)** - calculation of moles of NO at equilibrium **(1)** - calculation of moles of NO_2 at equilibrium **(1)**	<u>Example of calculation</u> = 7.000 ÷ 32 = 0.21875 / 0.219 (mol) Allow 7/32 = moles of oxygen x 2 = 0.4375 / 0.438 (mol) Allow 7/16 = total moles – moles of O_2 – moles of NO = 0.69625 – 0.21875 – 0.4375 = 0.0400 (mol) COMMENT: (a)(ii) may help with confusion about which number of moles goes with which molecule. If you cannot work out which goes with which award 1 mark for all 3, but as soon as 1 can be identified ignore other values which cannot Allow TE throughout Ignore SF	**(3)**

Question Number	Answer	Additional Guidance	Mark
15(a)(ii)		Example of calculation	**(4)**
	- divides the moles of the three substances by 15 to find the concentrations **(1)**	$[NO_2] = 0.0400 \div 15 = 0.0026667 / 2.6667 \times 10^{-3}$ (mol dm^{-3}) $[NO] = 0.4375 \div 15 = 0.029167 / 2.9167 \times 10^{-2}$ (mol dm^{-3}) $[O_2] = 0.21875 \div 15 = 0.014583 / 1.4583 \times 10^{-2}$ (mol dm^{-3}) Allow TE on incorrect values in (a)(i)	
	- gives the formula for K_c **(1)**	$= [NO_2]^2 \div [NO]^2[O_2]$ Allow an expression showing moles ÷ V for each substance Do not award round brackets Do not award K_p expressions	
	- substitution of concentrations in the expression given in M2 **(1)**	$K_c = 0.0026667^2 \div (0.029167^2 \times 0.014583)$ $K_c = 7.1113 \times 10^{-6} \div (8.5071 \times 10^{-4} \times 1.4583 \times 10^{-2})$ Award M2 for the correct expression if no formula has been given Allow TE on incorrect formula in M2 Allow TE on incorrect values calculated in M1 Allow TE on moles in (a)(i) used without converting to concentration	
	- calculation of final value including units **(1)**	$= 0.57320 / 5.7320 \times 10^{-1}$ dm^3 mol^{-1} / mol^{-1} dm^3 Allow TE on incorrect formula in M2 0.038213 dm^3 mol^{-1} (not ÷ 15) scores (3) 68.57 add Correct answer with some working scores (4) Ignore SF except 1 SF in final answer	

Question Number	Answer	Additional Guidance	Mark
15(b)	- rearrangement of $pV = nRT$ **(1)** - conversion of volume in dm^3 to m^3 **and** moles of gas = 0.69625 **(1)** - calculation of final value **(1)**	Example of calculation $T = pV \div nR$ Allow with values substituted in 15 dm^3 = 0.015 / 1.5×10^{-2} m^3 / 15×10^{-3} m^3 = (200,000 × 0.015) ÷ (0.69625 × 8.31) = 518.51 / 519 (K) Allow use of 8.314 rather than 8.31 Allow conversion of pressure to kPa and use of dm^3 giving = (200 × 15) ÷ (0.69625 × 8.31) = 518.51 / 519 (K) Allow 245.5(1) ºC / 246 ºC 518510 / 519000 (no conversion) scores (2) If given in ºC units must be given Allow TE on incorrect moles of gas and volume Do not award 518(K) or 519ºC Correct answer with some working scores (3) Ignore SF except 1 SF	**(3)**

Question Number	Answer	Additional Guidance	Mark
15(c)(i)	An answer that makes reference to the following point: • the reactants / NO and O_2 are colourless but the product / NO_2 is reddish brown / coloured	Allow just NO / O_2 is colourless and NO_2 is brown Allow just nitrogen dioxide / product is reddish brown / coloured / dark colour Allow any combination of yellow, red, orange and brown for the colour of NO_2 Allow measure the time for the brown gas to form Ignore just 'there will be a colour change' / mixture will darken Ignore NO_2 is a different colour form NO and O_2 Do not award NO is coloured so there is a colour change Do not award NO is yellow / red / orange / brown	**(1)**

Question Number	Answer	Additional Guidance	Mark
15(c)(ii)	• rearrangement of rate equation expression and inserting values **(1)** • calculation of *k* **and** units **(1)**	<u>Example of calculation</u> $= 6.87 \times 10^{-4} \div ((6.50 \times 10^{-2})^2 \times 1.25 \times 10^{-2})$ $= 13.008$ / $13.0\ \text{dm}^6\ \text{mol}^{-2}\ \text{s}^{-1}$ Correct answer with no working scores (2) Correct numerical answer with incorrect units scores (1) Allow units in any order Allow $\text{dm}^6/\text{mol}^2\text{s}$ 0.84554 / $0.846\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ (not squaring 6.50×10^{-2}) scores (1) for final value and units for M2 Ignore SF except 1SF	**(2)**

Question Number	Answer	Additional Guidance	Mark
15(c)(iii)	An answer that makes reference to the following point • a three particle collision is unlikely	Accept it is unlikely that more than two molecules will collide / Allow hard / difficult / impossible instead of unlikely Allow there are three molecules involved in the reaction Ignore it is a third order reaction Do not award just three moles colliding / just three reactants colliding	**(1)**

Question Number	Answer	Additional Guidance	Mark
15(c)(iv)	An answer that makes reference to the following points: • adding the two steps together gives the overall equation **(1)** • the steps do not match the rate equation because the slow step should be the second step **(1)**	Allow the two steps match the overall equation as the reactants and products are the same Allow N_2O_2 is formed then reacts / cancels out / is an intermediate Ignore just the overall equation is $2NO + O_2 \rightarrow 2NO_2$ Allow it does not match because there is no oxygen in the slow step / rate determining step / rds Allow because in this mechanism oxygen is zero order / is not first order Allow because with these steps the rate equation would be $rate = k[NO]^2$	**(2)**

(Total for Question 15 = 16 marks)

Question Number	Answer	Additional Guidance	Mark
16(a)(i)	 - calculation of the standard entropy of the reactants (1) - calculation of the standard entropy of the products (1) - calculation of the entropy change (products – reactants) (1)	Example of calculation COMMENT If enthalpy and entropy calculations are swapped allow max (2) scoring enthalpy calculation in enthalpy answer space and vice versa Penalise units once only $= 87.4 + (3 \times 197.6) = (680.2)$ (J K^{-1} mol^{-1}) $= (2 \times 27.3) + (3 \times 213.6) = (695.4)$ (J K^{-1} mol^{-1}) $= (695.4 - 680.2) = (+)15.2$ (J K^{-1} mol^{-1}) Ignore SF in final answer except 1 SF Correct answer with no working scores (3) Allow TE	**(3)**

Question Number	Answer	Additional Guidance	Mark
16(a)(ii)	• calculation of the standard enthalpy of formation of the reactants **(1)** • calculation of the standard enthalpy of formation of the products **(1)** • calculation of the enthalpy change (products – reactants) **(1)**	Example of calculation COMMENT If enthalpy and entropy calculations are swapped allow max (2) scoring enthalpy calculation in enthalpy answer space and vice versa = –824 + (3 × –111) = (–1157 (kJ mol^{-1})) = 3 × –394 = (–1182) (kJ mol^{-1}) = (–1182) – (–1157) = –25 (kJ mol^{-1}) –2339 (kJ mol^{-1}) scores M1 and M2 +25 (kJ mol^{-1}) scores M1 and M2 Ignore calculates the enthalpy change and then goes on to calculate $\Delta S_{\text{surroundings}}$ BUT allow the equations in (a)(iii) Ignore SF except 1 SF Correct answer with no working scores (3)	**(3)**

Question Number	Answer	Additional Guidance	Mark
16(a)(iii)	An answer that makes reference to the following points: Either (using entropy arguments) • $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$ **and** $\Delta S_{\text{surroundings}} = -\Delta H \div T$ **(1)** • (ΔH is negative so) $\Delta S_{\text{surroundings}}$ **or** $-\Delta H \div T$ is (always) positive **and** ΔS_{system} is positive **(1)** • ΔS_{total} is positive (at all temperatures) **and** so the reaction is feasible (at all temperatures) **(1)**	Candidates may use their values instead of symbols Penalise omission of Δ once only $\Delta S_{\text{total}} = \Delta S_{\text{system}} - \frac{\Delta H}{T}$ scores M1 Allow either equation described in words COMMENT These may be scored in (a)(ii) COMMENT If they have a +ve ΔH in (a)(ii), they must have -ve $\Delta S_{\text{surroundings}}$ (and ΔS_{system} is +ve) to score M2, but then cannot score M3 Allow spontaneous	**(3)**

	OR (using Gibbs free energy arguments) - $\Delta G = \Delta H - T\Delta S$ **(1)** - (ΔS is positive so) $T\Delta S$ **or** ΔS is (always) positive **and** ΔH is negative **(1)** - ΔG is (always) negative **and** so the reaction is (always) feasible **(1)**	Allow spontaneous Allow TE on values in (a)(i) and (a)(ii) Allow > 0 for positive and < 0 for negative throughout	

Question Number	Answer	Additional Guidance	Mark
16(b)(i)	An answer that makes reference to the following points:		**(4)**
	• calculation of ΔS_{system} **(1)**	$= ((2 \times 28.3) + (3 \times 213.6)) - (50.9 + (3 \times 197.6))$ $= 697.4 - 643.7$ $= 53.7$ (J K^{-1} mol)	
	• calculation of ΔH **(1)**	$= (3 \times -394) - (-1676 + (3 \times -111)$ $= -1182 + 2009$ $= 827$ (kJ mol^{-1})	
	• conversion of ΔS_{system} or ΔH so units match **(1)**	$\Delta S = 0.0537$ (kJ K^{-1} mol) or $\Delta H = 827000$ (J mol^{-1})	
	• rearrange $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$ when $\Delta S_{\text{total}} = 0$ and calculation of T **(1)**	$T = \Delta H \div \Delta S_{\text{system}}$ $= \frac{827000}{53.7} = 15400$ / $1.5400 \text{ x } 10^4$ (K) Correct answer scores (4) 15.4 (no M3) scores (3) Ignore incorrect units throughout except in final answer Allow TE thoughout except for M4 for a negative temperature	

Question Number	Answer	Additional Guidance	Mark
16(b)(ii)	An answer that makes reference to the following points: • because this temperature cannot be achieved in a Blast Furnace	COMMENT Unfortunately we cannot see (b)(i). Award only answers which suggest that the temperature is too high for the blast furnace to reach Allow the temperature in the Blast Furnace is too low Allow the temperature required is too high Ignore temperature required is very high Ignore the energy needed is too high Ignore activation energy is too high Ignore cost	**(1)**

(Total for Question 16 = 14 marks)

5 A group of students carried out a series of experiments to investigate the kinetics of the reaction between hydrogen peroxide and iodide ions in acidic conditions.

The equation for the reaction is shown.

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow 2H_2O(l) + I_2(aq)$$

Procedure

Step **1** Measure 10 cm^3 of aqueous sodium thiosulfate solution into a conical flask. Add 5 cm^3 of aqueous starch solution and 25 cm^3 of distilled water.

Step **2** Measure 5 cm^3 of aqueous potassium iodide solution and 5 cm^3 of dilute sulfuric acid and add these to the mixture in the conical flask from Step **1**.

Step **3** Measure 5 cm^3 of aqueous hydrogen peroxide solution into a test tube.

Step **4** Add the hydrogen peroxide solution to the conical flask, mix thoroughly and start the timer.

Step **5** Record the time when the solution turns blue-black.

Step **6** Repeat the experiment varying the volumes of aqueous potassium iodide solution and distilled water, keeping the total volume of the mixture constant.

(a) Explain the purpose of adding the sodium thiosulfate solution in Step **1**.

(2)

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....

(b) A set of results is shown.

Run	Volume of solutions / cm^3						Time (t) / s	1 / t / s^{-1}
	$Na_2S_2O_3$	Starch	H_2O	KI	H_2SO_4	H_2O_2		
1	10	5	25	5	5	5	270	0.0037
2	10	5	20	10	5	5	138	0.0072
3	10	5	15	15	5	5	93	0.011
4	10	5	10	20	5	5	71	0.014
5	10	5	5	25	5	5	55	0.018

(i) Plot a graph of 1 / t against the volume of potassium iodide.

(3)

(ii) Deduce the order of the reaction with respect to iodide ions, using your graph. Justify your answer.

(2)

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(c) Give a reason why the concentration of the potassium iodide solution is significantly lower than that of the hydrogen peroxide solution and the sulfuric acid.

(1)

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(Total for Question 5 = 8 marks)

TOTAL FOR PAPER = 50 MARKS

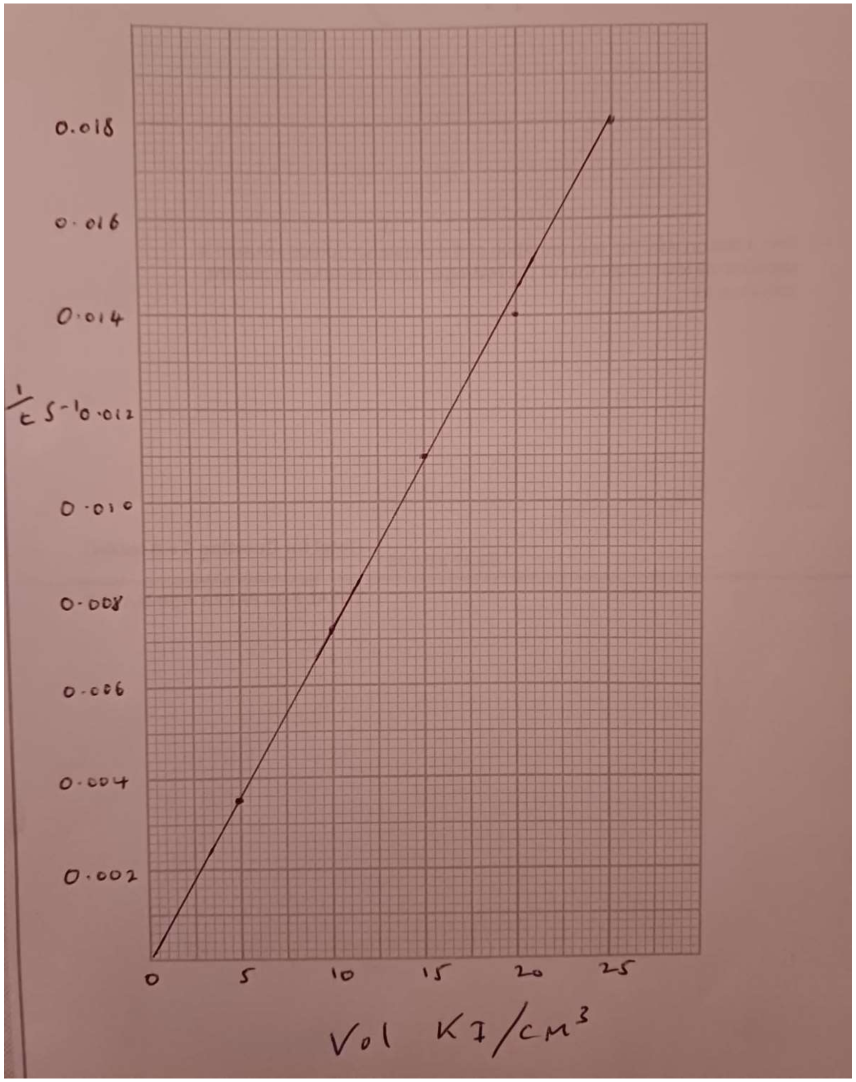
Question Number	Answer	Additional Guidance	Mark
5(a)	An answer that makes reference to the following points: - to react with the iodine formed **(1)** - so a colour change occurs when a certain amount of reaction has taken place **(1)** Standalone marks	Allow to remove the iodine Allow to reduce the iodine (to iodide ions) Allow balanced equation Allow to delay the colour change / solution turning blue-black Allow so the solution does not immediately change colour Allow when all the sodium thiosulfate is used up the iodine reacts with the starch/ there is a colour change (2) Do not award to slow down the reaction to delay the colour change	**(2)**

<table>
<tr><th>Question Number</th><th>Answer</th><th>Additional Guidance</th><th>Mark</th></tr>
<tr>
<td>**5(b)(i)**</td>
<td>

suitable axes and labels with units Axes wrong way round lose M1 **(1)**
points plotted correctly within half a square **(1)**
points joined with a straight line through the origin/would hit the origin if the line was extended Be lenient here as many have a scale that has no origin and so it will need estimating. Allow +/- two squares **(1)**

Points here for convenience

<table>
<tr><th>Volume</th><th>1/t s^{-1}</th></tr>
<tr><td>5</td><td>0.0037</td></tr>
<tr><td>10</td><td>0.0072</td></tr>
<tr><td>15</td><td>0.011</td></tr>
<tr><td>20</td><td>0.014</td></tr>
<tr><td>25</td><td>0.018</td></tr>
</table>

</td>
<td>
The points plotted must cover at least half the grid in both directions


</td>
<td>**(3)**</td>
</tr>
</table>

Question Number	Answer	Additional Guidance	Mark
5(b)(ii)	An answer that makes reference to the following points: • first order with respect to iodide ions **(1)** • because graph is a straight line through the origin **(1)**	Allow the graph (of rate and concentration) is a straight line/ linear Allow rate is proportional to concentration/volume Allow 1/t is proportional to concentration /volume Allow the relationship between two points Allow constant gradient	**(2)**

Question Number	Answer	Additional Guidance	Mark
5(c)	An answer that makes reference to the following point: • (the concentrations of hydrogen peroxide and sulfuric acid are effectively constant) so the rate is only dependent on the iodide ions/KI	Allow they (hydrogen peroxide and sulfuric acid) do not affect the rate Ignore iodide ions are the only variable/only the concentration of iodide ions is changing	**(1)**

(Total for Question 5 = 8 marks)
(Total for Paper = 50 marks)

Version 2

Edexcel IAL 2023 Oct - 2025 Jun

15 A reaction vessel contained nitrogen monoxide and oxygen in a 2 : 1 molar ratio. The mixture was allowed to come to equilibrium forming nitrogen dioxide. The equation for the reaction is shown.

$$2NO + O_2 \rightleftharpoons 2NO_2$$

The volume of the vessel was 15 dm^3 and the reaction was carried out at a constant temperature and at a pressure of 200 000 Pa.

At equilibrium there was a total of 0.69625 mol of gas in the reaction vessel and the mass of oxygen was 7.000 g.

(a) (i) Calculate the number of moles of each substance at equilibrium.

(3)

(ii) Calculate the value of K_c under these conditions. Include units in your answer.

(4)

DO NOT WRITE IN THIS AREA DO NOT WRITE IN THIS AREA DO NOT WRITE IN THIS AREA

(b) Calculate the temperature, in *K*, of the reaction mixture at equilibrium under these conditions.
Use the equation $pV = nRT$ and the data at the start of the question.

(3)

(c) Under a different set of conditions, the reaction was carried out to find the initial rate of reaction.

Experiment number	Initial [NO] / mol dm^{-3}	Initial [O_2] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	6.50×10^{-2}	1.25×10^{-2}	6.87×10^{-4}

The rate equation for this reaction is

$$\text{rate} = k[\text{NO}]^2[\text{O}_2]$$

(i) Give the reason why colorimetry can be used to monitor the rate of the reaction.

(1)

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....

....

(ii) Use the data from Experiment 1 to find the value of the rate constant, *k*. Include units in your answer.

(2)

(iii) State why the reaction is unlikely to proceed in a single step.

(1)

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....

....

(iv) A student proposed the mechanism shown for this reaction.

$$2NO \rightleftharpoons N_2O_2 \qquad \text{slow}$$

$$N_2O_2 + O_2 \rightarrow 2NO_2 \qquad \text{fast}$$

Justify whether or not this mechanism is consistent with the overall equation for the reaction **and** with the rate equation.

(2)

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(Total for Question 15 = 16 marks)

16 Iron, lead and zinc can be extracted using a blast furnace but aluminium cannot.

In a blast furnace, iron is extracted from iron(III) oxide, Fe_2O_3, at high temperature.

Some standard enthalpy changes of formation, $\Delta_f H^\ominus$, and standard molar entropies, $S^\ominus$, are shown.

Substance	Al(s)	Al_2O_3(s)	CO(g)	CO_2(g)	Fe(s)	Fe_2O_3(s)
$\Delta_f H^\ominus$ / kJ mol^{-1}	0	–1676	–111	–394	0	–824
$S^\ominus$ / J K^{-1} mol^{-1}	28.3	50.9	197.6	213.6	27.3	87.4

(a) The main reaction occurring in the blast furnace to form iron is shown.

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$$

This reaction is feasible at all temperatures.

(i) Calculate the standard entropy change of the system for this reaction.

(3)

(ii) Calculate the standard enthalpy change for this reaction.

(3)

(iii) Explain how your answers to (a)(i) and (a)(ii) show that this reaction is feasible at all temperatures.

(3)

(b) The main reduction reaction of aluminium oxide in a blast furnace is shown.

$$Al_2O_3 + 3CO \rightarrow 2Al + 3CO_2$$

(i) Calculate the temperature at which this reaction becomes feasible.

(4)

(ii) Suggest why aluminium is not extracted from its oxide using a blast furnace.

(1)

(Total for Question 16 = 14 marks)

Question Number	Answer	Additional Guidance	Mark
15(a)(i)	- calculation of moles of oxygen at equilibrium **(1)** - calculation of moles of NO at equilibrium **(1)** - calculation of moles of NO_2 at equilibrium **(1)**	<u>Example of calculation</u> = 7.000 ÷ 32 = 0.21875 / 0.219 (mol) Allow 7/32 = moles of oxygen x 2 = 0.4375 / 0.438 (mol) Allow 7/16 = total moles – moles of O_2 – moles of NO = 0.69625 – 0.21875 – 0.4375 = 0.0400 (mol) COMMENT: (a)(ii) may help with confusion about which number of moles goes with which molecule. If you cannot work out which goes with which award 1 mark for all 3, but as soon as 1 can be identified ignore other values which cannot Allow TE throughout Ignore SF	**(3)**

Question Number	Answer	Additional Guidance	Mark
15(a)(ii)		Example of calculation	**(4)**
	- divides the moles of the three substances by 15 to find the concentrations **(1)**	$[NO_2]$ = 0.0400 ÷ 15 = 0.0026667 / 2.6667×10^{-3} (mol dm^{-3}) $[NO]$ = 0.4375 ÷ 15 = 0.029167 / 2.9167×10^{-2} (mol dm^{-3}) $[O_2]$ = 0.21875 ÷ 15 = 0.014583 / 1.4583×10^{-2} (mol dm^{-3}) Allow TE on incorrect values in (a)(i)	
	- gives the formula for K_c **(1)**	$= [NO_2]^2 \div [NO]^2[O_2]$ Allow an expression showing moles ÷ V for each substance Do not award round brackets Do not award K_p expressions	
	- substitution of concentrations in the expression given in M2 **(1)**	$K_c = 0.0026667^2 \div (0.029167^2 \times 0.014583)$ $K_c = 7.1113 \times 10^{-6} \div (8.5071 \times 10^{-4} \times 1.4583 \times 10^{-2})$ Award M2 for the correct expression if no formula has been given Allow TE on incorrect formula in M2 Allow TE on incorrect values calculated in M1 Allow TE on moles in (a)(i) used without converting to concentration	
	- calculation of final value including units **(1)**	= 0.57320 / 5.7320×10^{-1} $dm^3\ mol^{-1}$ / $mol^{-1}\ dm^3$ Allow TE on incorrect formula in M2 0.038213 $dm^3\ mol^{-1}$ (not ÷ 15) scores (3) 68.57 add Correct answer with some working scores (4) Ignore SF except 1 SF in final answer	

Question Number	Answer	Additional Guidance	Mark
15(b)		Example of calculation	(3)
	• rearrangement of $pV = nRT$ **(1)**	$T = pV \div nR$ Allow with values substituted in	
	• conversion of volume in dm^3 to m^3 **and** moles of gas = 0.69625 **(1)**	15 dm^3 = 0.015 / 1.5×10^{-2} m^3 / 15×10^{-3} m^3	
	• calculation of final value **(1)**	= (200,000 × 0.015) ÷ (0.69625 × 8.31) = 518.51 / 519 (K) Allow use of 8.314 rather than 8.31 Allow conversion of pressure to kPa and use of dm^3 giving = (200 × 15) ÷ (0.69625 × 8.31) = 518.51 / 519 (K) Allow 245.5(1) ºC / 246 ºC 518510 / 519000 (no conversion) scores (2) If given in ºC units must be given Allow TE on incorrect moles of gas and volume Do not award 518(K) or 519ºC Correct answer with some working scores (3) Ignore SF except 1 SF	

Question Number	Answer	Additional Guidance	Mark
15(c)(i)	An answer that makes reference to the following point: - the reactants / NO and O_2 are colourless but the product / NO_2 is reddish brown / coloured	Allow just NO / O_2 is colourless and NO_2 is brown Allow just nitrogen dioxide / product is reddish brown / coloured / dark colour Allow any combination of yellow, red, orange and brown for the colour of NO_2 Allow measure the time for the brown gas to form Ignore just 'there will be a colour change' / mixture will darken Ignore NO_2 is a different colour form NO and O_2 Do not award NO is coloured so there is a colour change Do not award NO is yellow / red / orange / brown	**(1)**

Question Number	Answer	Additional Guidance	Mark
15(c)(ii)	- rearrangement of rate equation expression and inserting values **(1)** - calculation of *k* **and** units **(1)**	<u>Example of calculation</u> $= 6.87 \text{ x } 10^{-4} \div ((6.50 \times 10^{-2})^2 \text{ x } 1.25 \times 10^{-2})$ $= 13.008 / 13.0 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ Correct answer with no working scores (2) Correct numerical answer with incorrect units scores (1) Allow units in any order Allow $\text{dm}^6/\text{mol}^2\text{s}$ $0.84554 / 0.846 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (not squaring 6.50×10^{-2}) scores (1) for final value and units for M2 Ignore SF except 1SF	**(2)**

Question Number	Answer	Additional Guidance	Mark
15(c)(iii)	An answer that makes reference to the following point • a three particle collision is unlikely	Accept it is unlikely that more than two molecules will collide / Allow hard / difficult / impossible instead of unlikely Allow there are three molecules involved in the reaction Ignore it is a third order reaction Do not award just three moles colliding / just three reactants colliding	**(1)**

Question Number	Answer	Additional Guidance	Mark
15(c)(iv)	An answer that makes reference to the following points: • adding the two steps together gives the overall equation **(1)**	Allow the two steps match the overall equation as the reactants and products are the same Allow N_2O_2 is formed then reacts / cancels out / is an intermediate Ignore just the overall equation is $2NO + O_2 \rightarrow 2NO_2$	**(2)**
	• the steps do not match the rate equation because the slow step should be the second step **(1)**	Allow it does not match because there is no oxygen in the slow step / rate determining step / rds Allow because in this mechanism oxygen is zero order / is not first order Allow because with these steps the rate equation would be $rate = k[NO]^2$	

(Total for Question 15 = 16 marks)

Question Number	Answer		Additional Guidance	Mark
16(a)(i)			Example of calculation COMMENT If enthalpy and entropy calculations are swapped allow max (2) scoring enthalpy calculation in enthalpy answer space and vice versa Penalise units once only	**(3)**
	• calculation of the standard entropy of the reactants	(1)	$= 87.4 + (3 \times 197.6) = (680.2)$ (J K^{-1} mol^{-1})	
	• calculation of the standard entropy of the products	(1)	$= (2 \times 27.3) + (3 \times 213.6) = (695.4)$ (J K^{-1} mol^{-1})	
	• calculation of the entropy change (products – reactants)	(1)	$= (695.4 - 680.2) = (+)15.2$ (J K^{-1} mol^{-1})	
			Ignore SF in final answer except 1 SF Correct answer with no working scores (3) Allow TE	

Question Number	Answer	Additional Guidance	Mark
16(a)(ii)	 - calculation of the standard enthalpy of formation of the reactants **(1)** - calculation of the standard enthalpy of formation of the products **(1)** - calculation of the enthalpy change (products – reactants) **(1)**	Example of calculation COMMENT If enthalpy and entropy calculations are swapped allow max (2) scoring enthalpy calculation in enthalpy answer space and vice versa = –824 + (3 × –111) = (–1157 (kJ mol^{-1})) = 3 × –394 = (–1182) (kJ mol^{-1}) = (–1182) – (–1157) = –25 (kJ mol^{-1}) –2339 (kJ mol^{-1}) scores M1 and M2 +25 (kJ mol^{-1}) scores M1 and M2 Ignore calculates the enthalpy change and then goes on to calculate $\Delta S_{\text{surroundings}}$ BUT allow the equations in (a)(iii) Ignore SF except 1 SF Correct answer with no working scores (3)	**(3)**

Question Number	Answer	Additional Guidance	Mark
16(a)(iii)	An answer that makes reference to the following points: Either (using entropy arguments) • $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$ **and** $\Delta S_{\text{surroundings}} = -\Delta H \div T$ **(1)** • (ΔH is negative so) $\Delta S_{\text{surroundings}}$ **or** $-\Delta H \div T$ is (always) positive **and** ΔS_{system} is positive **(1)** • ΔS_{total} is positive (at all temperatures) **and** so the reaction is feasible (at all temperatures) **(1)**	Candidates may use their values instead of symbols Penalise omission of Δ once only $\Delta S_{\text{total}} = \Delta S_{\text{system}} - \frac{\Delta H}{T}$ scores M1 Allow either equation described in words COMMENT These may be scored in (a)(ii) COMMENT If they have a +ve ΔH in (a)(ii), they must have -ve $\Delta S_{\text{surroundings}}$ (and ΔS_{system} is +ve) to score M2, but then cannot score M3 Allow spontaneous	**(3)**

	OR (using Gibbs free energy arguments) • $\Delta G = \Delta H - T\Delta S$ **(1)** • (ΔS is positive so) $T\Delta S$ **or** ΔS is (always) positive **and** ΔH is negative **(1)** • ΔG is (always) negative **and** so the reaction is (always) feasible **(1)**	Allow spontaneous Allow TE on values in (a)(i) and (a)(ii) Allow > 0 for positive and < 0 for negative throughout	

Question Number	Answer	Additional Guidance	Mark
16(b)(i)	An answer that makes reference to the following points:		**(4)**
	• calculation of ΔS_{system} **(1)**	$= ((2 \times 28.3) + (3 \times 213.6)) - (50.9 + (3 \times 197.6))$ $= 697.4 - 643.7$ $= 53.7$ (J K^{-1} mol)	
	• calculation of ΔH **(1)**	$= (3 \times -394) - (-1676 + (3 \times -111))$ $= -1182 + 2009$ $= 827$ (kJ mol^{-1})	
	• conversion of ΔS_{system} or ΔH so units match **(1)**	$\Delta S = 0.0537$ (kJ K^{-1} mol) or $\Delta H = 827000$ (J mol^{-1})	
	• rearrange $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$ when $\Delta S_{\text{total}} = 0$ and calculation of T **(1)**	$T = \Delta H \div \Delta S_{\text{system}}$ $= \frac{827000}{53.7} = 15400$ / $1.5400 \text{ x } 10^4$ (K) Correct answer scores (4) 15.4 (no M3) scores (3) Ignore incorrect units throughout except in final answer Allow TE thoughout except for M4 for a negative temperature	

Question Number	Answer	Additional Guidance	Mark
16(b)(ii)	An answer that makes reference to the following points: • because this temperature cannot be achieved in a Blast Furnace	COMMENT Unfortunately we cannot see (b)(i). Award only answers which suggest that the temperature is too high for the blast furnace to reach Allow the temperature in the Blast Furnace is too low Allow the temperature required is too high Ignore temperature required is very high Ignore the energy needed is too high Ignore activation energy is too high Ignore cost	**(1)**

(Total for Question 16 = 14 marks)

SECTION B

Answer ALL the questions. Write your answers in the spaces provided.

16 A group of students investigated the kinetics of a ‘clock’ reaction.

The reaction investigated was that between hydrogen peroxide and iodide ions in the presence of acid.

Reaction 1 $H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow 2H_2O(l) + I_2(aq)$

In this ‘clock’ reaction, a fixed volume of aqueous sodium thiosulfate, $Na_2S_2O_3$, and a small amount of starch were added to the reaction mixture.

The added thiosulfate ions react with the iodine produced in **Reaction 1**.

Reaction 2 $2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$

When all the thiosulfate ions have reacted, the presence of iodine is detected by the formation of a starch-iodine complex. The students recorded the time taken for this complex to form.

(a) (i) State the final colour of the mixture containing the starch-iodine complex.

(1)

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(ii) Under appropriate conditions, the reciprocal of time can be used as an approximate measure of the initial rate of the reaction.

Explain why the concentration of the sodium thiosulfate must be low compared with the initial concentrations of the other reagents.

(2)

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(b) Four reaction mixtures, with different initial concentrations of hydrogen peroxide, hydrogen ions and iodide ions, were prepared.

Each mixture had the same volume and contained the same amount of sodium thiosulfate and starch.

Mixture	$[H_2O_2]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	$[I^-]$ / mol dm^{-3}	Time / s	1 ÷ time / s^{-1}
1	5.4×10^{-2}	1.7×10^{-5}	8.2×10^{-3}	195	5.13×10^{-3}
2	2.7×10^{-2}	1.7×10^{-5}	8.2×10^{-3}	391	2.56×10^{-3}
3	5.4×10^{-2}	1.7×10^{-5}	1.6×10^{-2}	97	1.03×10^{-2}
4	5.4×10^{-2}	1.7×10^{-4}	8.2×10^{-3}	204	4.90×10^{-3}

(i) Use the results in the table to deduce the order of **Reaction 1** with respect to hydrogen peroxide, hydrogen ions and iodide ions.
Justify each answer by referring to relevant data from the table.

(3)

Hydrogen peroxide ....

....

Hydrogen ions ....

....

Iodide ions ....

....

(ii) Write the overall rate equation for **Reaction 1** using your answers to (b)(i).

(1)

(iii) All four mixtures contained 8.50×10^{-5} mol of sodium thiosulfate.
Calculate the amount of iodine that had reacted with the sodium thiosulfate when the colour changed in **Reaction 2**.

(1)

(iv) Calculate the rate of reaction, in mol dm^{-3} s^{-1}, with respect to **hydrogen peroxide** using the answer from (b)(iii), the stoichiometry of **Reaction 1** and data from Mixture 1.
The total volume of **each** Mixture was 0.050 dm^{3}.

(2)

(v) Calculate a value for the rate constant of **Reaction 1** using data from Mixture 1 and your answers to (b)(ii) and (b)(iv).
Include the units of the rate constant.

(2)

(c) The activation energy for **Reaction 1** may be found by repeating the experiment at different temperatures.
Each student carried out an experiment at a different temperature.
One of the students misread the thermometer in their experiment.

ln rate	T / K	$1 \div T$ / K^{-1}
–1.8	333	0.00300
–2.5	323	0.00310
–3.6	308	0.00325
–4.0	307	0.00326
–4.7	291.5	0.00343
–6.0	278	0.00360

The activation energy, E_a, for a reaction may be found by plotting a graph of ln rate against $1/T$.
The gradient of the resulting line of best fit can be used in the Arrhenius equation to determine a value for E_a, in kJ mol^{-1}.

(i) Determine the value for E_a for **Reaction 1** by plotting a graph using the axes provided.
You should take into account the error made by one of the students.

$$\ln \text{rate} = -\frac{E_a}{R} \times \frac{1}{T} + \text{constant} \qquad R = 8.31\ \text{J K}^{-1}\ \text{mol}^{-1}$$

(5)

E_a .... kJ mol^{-1}

(ii) The students all used thermometers capable of reading to the same precision. Use your graph to deduce the temperature that the student who made the error should have read on their thermometer.

(2)

(Total for Question 16 = 19 marks)

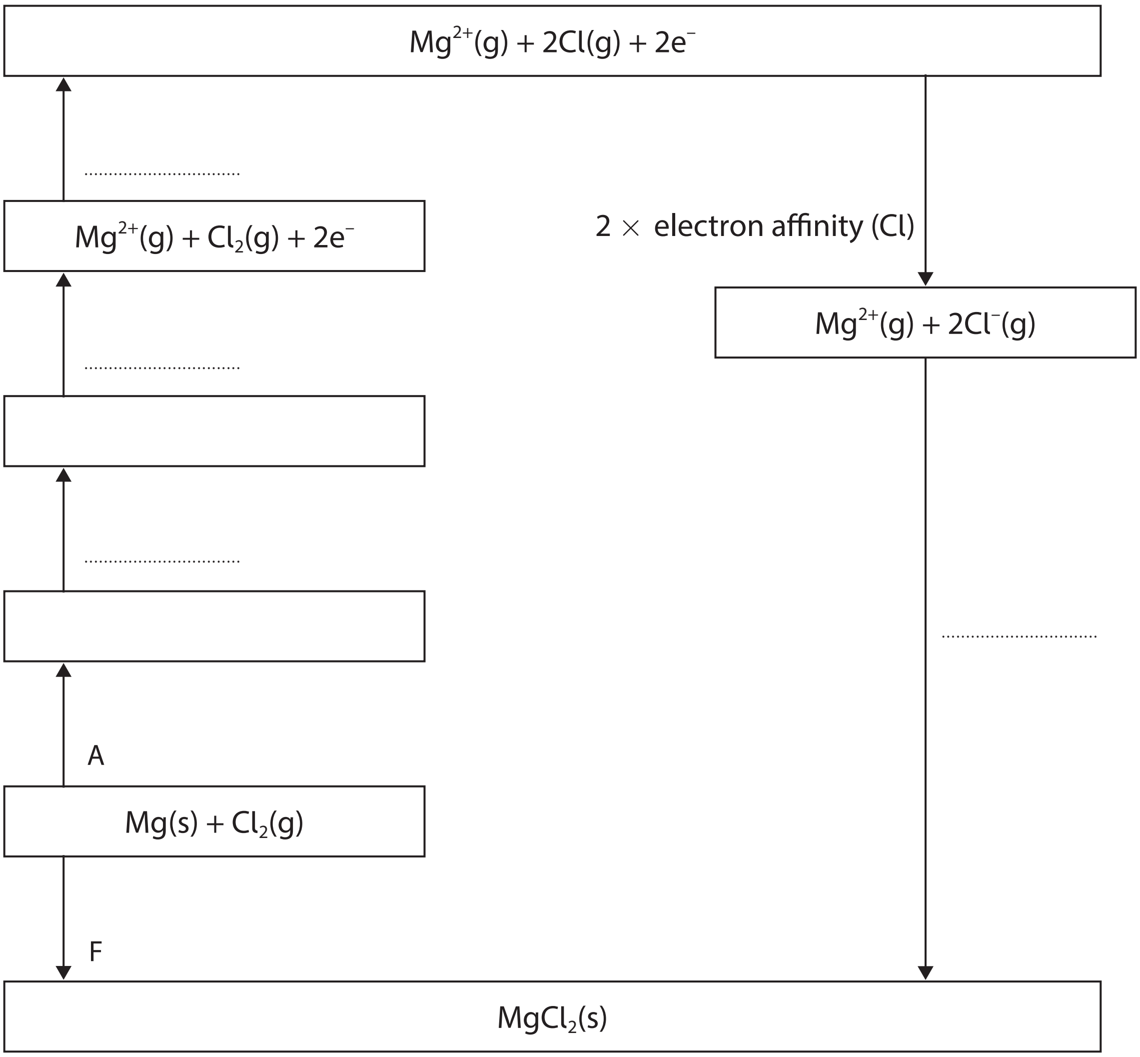
17 The question is about lattice energies.

The table shows energy values used in a Born–Haber cycle for magnesium chloride, $MgCl_2$.

Energy change	Label	Value / kJ mol^{-1}
Enthalpy change of atomisation of magnesium	A	+148
First ionisation energy of magnesium	B	+738
Second ionisation energy of magnesium	C	+1451
Enthalpy change of atomisation of chlorine	D	+122
Lattice energy of magnesium chloride	E	–2526
Enthalpy change of formation of magnesium chloride	F	–641

(a) (i) Complete the Born–Haber cycle for magnesium chloride by adding labels for each of the four energy changes and writing formulae in the two empty boxes.

(3)



(ii) Calculate a value for the electron affinity of chlorine, in kJ mol^{-1}, using the data in the table and the completed Born–Haber cycle.

(2)

(iii) Explain why, when magnesium reacts with chlorine, $MgCl_2$ is formed rather than $MgCl_3$.

(2)

....

....

....

....

....

(iv) Calculate the standard molar enthalpy change of solution of magnesium chloride, in kJ mol^{-1}, using the data shown and the value for the lattice energy, LE[$MgCl_2$], given in the table.

Data $\Delta_{hyd}H^{\ominus}[Mg^{2+}(g)] = -1920\ kJ\ mol^{-1}$ $\Delta_{hyd}H^{\ominus}[Cl^{-}(g)] = -364\ kJ\ mol^{-1}$

(2)

*(b) Lattice energies from the Born–Haber cycle are based on experimental values. Theoretical lattice energies can also be calculated. Experimental and theoretical values for three different crystal lattices are shown.

Compound	Experimental lattice energy / kJ mol^{-1}	Theoretical lattice energy / kJ mol^{-1}
sodium fluoride NaF	–918	–912
magnesium fluoride MgF_2	–2957	–2913
magnesium chloride $MgCl_2$	–2526	–2326

Discuss the reasons for the differences in these six values of lattice energy in terms of the structure and bonding in these three substances.

(6)

(Total for Question 17 = 15 marks)

Section B

Question Number	Answer	Additional Guidance	Mark
16(a)(i)	An answer that makes reference to the following point: • Blue(-)black	Accept (dark) blue /black/ black-blue	**(1)**

Question Number	Answer	Additional Guidance	Mark
16(a)(ii)	An explanation that makes reference to the following points: • the thiosulfate must be used up (before the concentration of the other reagents change significantly) (1) • so the rate is unaffected by changes in concentration of the reagents during the reaction (1)	Allow the thiosulfate/it reacts completely/Reaction 1 is complete/ there must be (some) iodine produced to react with starch Allow (before) the concentration of the other reactants changes appreciably/so that the concentration of other reactants does not change much/so that the initial rate is determined If no other mark scored allow : if the concentration is high then no iodine produced / no complex formed/no colour change scores 1 Do not award references to an increase in the rate of the reaction of sodium thiosulfate and iodine if the concentration is high.	**(2)**

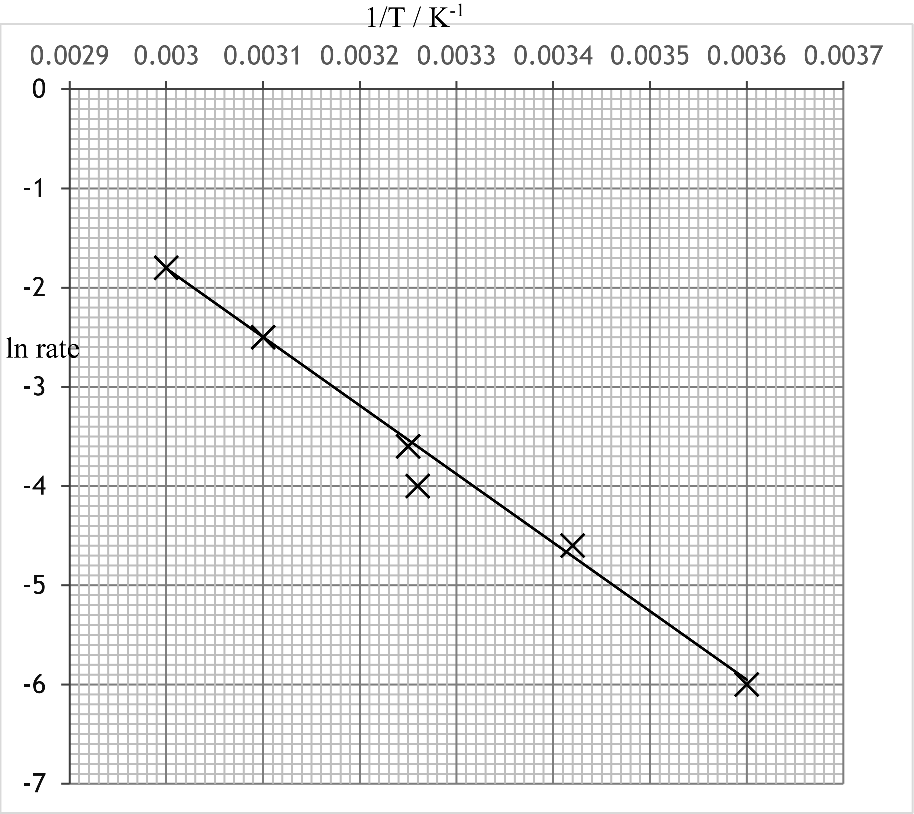
Question Number	Answer	Additional Guidance	Mark
16(b)(i)	An answer that makes reference to three of the following points: • (reaction is) first order in hydrogen peroxide because as the concentration is halved, the reciprocal of time/the rate is halved **(1)** • (reaction is) zero order in hydrogen ions as the rate does not change with a change in concentration of hydrogen ions **(1)** • (reaction is) first order in iodide ions because as the concentration is doubled the reciprocal of time/rate is doubled **(1)**	Marks can be scored from annotation on table Allow as the concentration of hydrogen peroxide is halved (changed in mixtures one and two) the time is doubled Allow reverse argument Allow as the concentration of hydrogen ions is changed (between mixtures one and four) (by a factor of ten) there is little/no change in rate Allow as the concentration of iodide ions is doubled (in mixtures one and three) the time is halved Allow reverse argument If no other mark is scored award one mark if all three orders of reaction are correct with no or incorrect justification.	**(3)**

Question Number	Answer	Additional Guidance	Mark
16(b)(ii)	An answer that makes reference to the following point: • rate = $k[H_2O_2][I^-]$	Allow rate = $k[H_2O_2][I^-][H^+]^0$ Allow species in any order TE from (b)(i)	**(1)**

Question Number	Answer	Additional Guidance	Mark
16(b)(iii)	- calculation of the amount of iodine which reacted with the thiosulfate	<u>Example of calculation</u> $8.50 \times 10^{-5} \div 2 = 4.25 \times 10^{-5}$ (mol) Correct answer with no working scores 1 Ignore SF except 1 SF	**(1)**

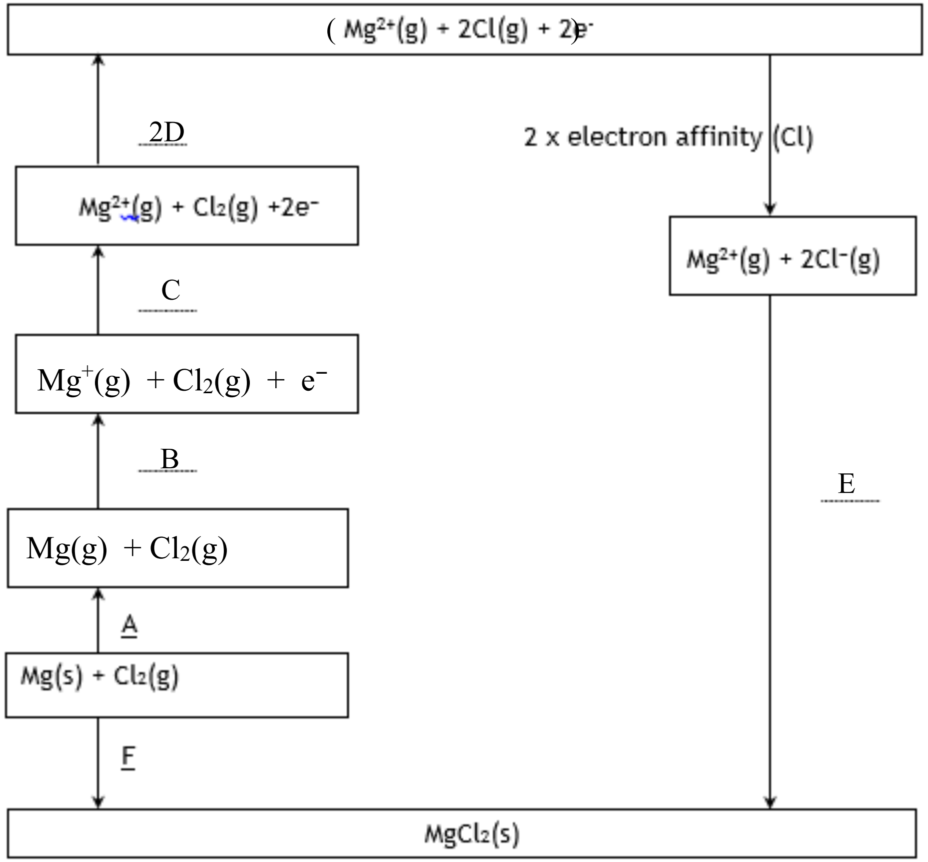
Question Number	Answer	Additional Guidance	Mark
16(b)(iv)	- calculation of rate of loss of amount of iodine / loss of hydrogen peroxide in mols **(1)** - calculation of reaction rate in mol dm^{-3} s^{-1}) **(1)**	<u>Example of calculation</u> $4.25 \times 10^{-5} \div 195 = 2.1795 / 2.18 / 2.2 \times 10^{-7}$ (mol s^{-1}) $2.1795 \times 10^{-7} \div 0.05 = 4.3590/4.36/4.4 \times 10^{-6}$ (mol dm^{-3} s^{-1}) Correct answer with no working scores 2 Ignore SF except 1SF TE from (iii)	**(2)**

Question Number	Answer	Additional Guidance	Mark
16(b)(v)	• rearrangement of the rate equation and calculation of the rate constant **(1)** • units **(1)**	Example of calculation k = rate ÷ ($[H_2O_2] \times [I^-]$) $k = 4.359 \times 10^{-6} \div (5.4 \times 10^{-2} \times 8.2 \times 10^{-3})$ $= 4.359 \times 10^{-6} \div 4.428 \times 10^{-4}$ $= 9.844 \times 10^{-3}$ Ignore SF except 1SF $dm^3\ mol^{-1}\ s^{-1}$ Accept units in any order Correct answer with no working and units scores 2 TE from (ii) (iii) and (iv)	**(2)**

Question Number	Answer	Additional Guidance	Mark
16(c)(i)	- axes correct with scales allowing plot to cover at least half the grid and ln rate values becoming more negative down the axis **(1)** - both axes labelled with units K^{-1} on x axis **(1)** - points correctly plotted and best fit line drawn **(1)** - gradient in the range −7200 to −6800 **(1)** - $E_a = -(-7000 \times 8.31) \div 1000$ $= +58.2$ ($kJ\ mol^{-1}$) range 56.5 to 59.9 **(1)** TE on incorrect gradient value but Ea must be positive Ignore SF except 1 SF	Example of calculation Allow horizontal axis at bottom of graph Ignore extrapolation  Allow plotting of all points except the incorrect one TE on incorrect gradient Ignore SF	**(5)**

Question Number	Answer	Additional Guidance	Mark
16(c)(ii)	An explanation that makes reference to the following points: • correct value of 1/T from the graph **(1)** • conversion to temperature **(1)**	0.00331 ± 0.00001 302K (Range 301K -303K) TE from incorrect 1/T read from graph Ignore SF	**(2)**

(Total for Question 16 = 19 marks)

Question Number	Answer	Additional Guidance	Mark
17(a)(i)	An answer that makes reference to six of the following points: Clockwise from enthalpy change A • $Mg(g) + Cl_2(g)$ **(1)** • B / (+)738 **(1)** • $Mg^+(g) + Cl_2(g) + e^-$ **(1)** • C/ (+)1451 **(1)** • 2D / (+)244 **(1)** • E / (-)2526 **(1)** All 6 points correct three marks 4/5 points correct two marks 2/3 points correct one mark	 Allow any unambiguous labels for the arrows including words or values If the value is given correctly ignore an incorrect letter. Penalise missing or incorrect state symbol once only	**(3)**

Question Number	Answer	Additional Guidance	Mark
17(a)(ii)	- correct expression **(1)** - correct rearrangement **and** evaluation of 1st electron affinity of chlorine **(1)**	<u>Example of calculation</u> $-641 = 148 + 738 + 1451 + (2 \times 122) + 2EACl_2 - 2526$ $2EACl_2 = -641 - (148 + 738 + 1451 + (2 \times 122)) + 2526$ $= -696$ $\Delta H(EA\text{chlorine}) = -696 \div 2 = -348$ (kJ mol^{-1}) Correct answer with no working scores 2 No TE on incorrect expression except Failure to multiply atomisation energy by 2 i.e. $2EACl_2 = -574$ (kJ mol^{-1}) and then $\Delta H(EA\text{chlorine}) = -574 \div 2 = -287$ (kJ mol^{-1}) for 1 mark	**(2)**

Question Number	Answer	Additional Guidance	Mark
17(a)(iii)	An explanation that makes reference to the following points: - the third ionisation energy for magnesium is very high (because the third electron is being removed from the 2p orbital / an inner shell) **(1)** - which would not be compensated for by the lattice energy **(1)**	Allow the enthalpy of formation of $MgCl_3$ would be (highly) endothermic/the energy released when $MgCl_3$ is formed would need to be more than that released when $MgCl_2$ forms	**(2)**

Question Number	Answer	Additional Guidance	Mark
17(a)(iv)	- calculation of the combined hydration enthalpies of the gaseous ions **(1)** - subtraction of the lattice energy of the solid **(1)**	Example of calculation $-1920-2(364) = -2648$ (kJ mol^{-1}) $-2648 - -2526 = -122$ (kJ mol^{-1}) Correct answer scores 2 Sign reversed (+)122 scores 1	**(2)**

<table>
<tr><th>Question Number</th><th>Answer</th><th>Additional Guidance</th><th>Mark</th></tr>
<tr>
<td>*17(b)</td>
<td>
<p>This question assesses the student’s ability to show a coherent and logically structured answer with linkages and fully sustained reasoning.</p>
<p>Marks are awarded for indicative content and for how the answer is structured and shows lines of reasoning.</p>
<p>The following table shows how the marks should be awarded for indicative content.</p>
<table>
<tr><td>Number of indicative marking points seen in answer</td><td>Number of marks awarded for indicative marking points</td></tr>
<tr><td>6</td><td>4</td></tr>
<tr><td>5-4</td><td>3</td></tr>
<tr><td>3-2</td><td>2</td></tr>
<tr><td>1</td><td>1</td></tr>
<tr><td>0</td><td>0</td></tr>
</table>
<p>The following table shows how the marks should be awarded for structure and lines of reasoning</p>
<table>
<tr><td></td><td>Number of marks awarded for structure of answer and sustained lines of reasoning</td></tr>
<tr><td>Answer shows a coherent logical structure with linkages and fully sustained lines of reasoning demonstrated throughout</td><td>2</td></tr>
<tr><td>Answer is partially structured with some linkages and lines of reasoning</td><td>1</td></tr>
<tr><td>Answer has no linkages between points and is unstructured</td><td>0</td></tr>
</table>
</td>
<td>
<p>Guidance on how the mark scheme should be applied.</p>
<p>The mark for indicative content should be added to the mark for lines of reasoning. For example, a response with five indicative marking points that is partially structured with some linkages and lines of reasoning scores 4 marks (3 marks for indicative content and 1 mark for partial structure and some linkages and lines of reasoning).</p>
<p>If there were no linkages between the points, then the same indicative marking points would yield an overall score of 3 marks (3 marks for indicative content and no marks for linkages).</p>
<p>In general it would be expected that
5 or 6 indicative points would get 2 reasoning marks
3 or 4 indicative points would get 1 reasoning mark
0, 1 or 2 indicative points would get zero reasoning marks</p>
<p>If there is any incorrect chemistry, deduct mark(s) from the reasoning. If no reasoning mark(s) awarded do not deduct mark(s).</p>
<p>Comment: Look for the indicative marking points first, then consider the mark for the structure of the answer and sustained line of reasoning</p>
</td>
<td>(6)</td>
</tr>
</table>

	Indicative content **IP1** The magnesium (ion) has larger charge/smaller **ionic** radius than the sodium (ion) **IP2** The attraction between the ions/ionic bond is stronger in magnesium fluoride (so lattice energies of sodium fluoride are less exothermic) **IP3** The magnesium ion is more polarising than the sodium ion **IP4** The chloride ion is larger/ more polarisable than the fluoride ion **IP5** The difference between theoretical and experimental values is greatest for magnesium chloride / the difference between theoretical and experimental values is least for sodium fluoride **IP6** Magnesium chloride has the greatest degree of covalent character/Sodium fluoride has the greatest degree of ionic character	Allow reverse arguments throughout Allow sodium ion has 1+ charge and magnesium ion has 2+charge/sodium has smaller charge density than magnesium Cannot get this mark just for comparing values in table Magnesium ion causes more distortion of anion than sodium ion Accept the electronegativity **difference** between sodium and fluorine is greater than that between magnesium and chlorine Allow $MgCl_2$ has more covalent character than NaF Allow NaF is 100% ionic and $MgCl_2$ is partially covalent Ignore references to the number of bonds mention of intermolecular forces loses 1 reasoning mark	

(Total for Question 17 = 15 marks)

SECTION B

Answer ALL the questions. Write your answers in the spaces provided.

15 This question is about some compounds of silicon.

(a) Silicon dioxide and magnesium react when heated strongly.

Reaction **1** $SiO_2(s) + 4Mg(s) \rightarrow Mg_2Si(s) + 2MgO(s)$

(i) Complete the table, indicating the type of bonding in the reactants and products of this reaction.

(2)

Substance	SiO_2	Mg	Mg_2Si	MgO
Bonding type			covalent	

(ii) The entropy change of the system, ΔS_{system}, for Reaction **1** is –43.8 J K^{-1} mol^{-1}.

Suggest, with reference to the equation, why ΔS_{system} for this reaction is negative.

(2)

....

....

....

....

....

(iii) The enthalpy change, ΔH, for Reaction **1** is –370 kJ mol^{-1}.

Calculate the entropy change of the surroundings, $\Delta S_{surroundings}$, in J K^{-1} mol^{-1}, for Reaction **1** at 23.0 °C.

(2)

(iv) Calculate the total entropy change, ΔS_{total}, for Reaction **1** at 23.0 °C.

Give your answer to an appropriate number of significant figures, and in units of $J K^{-1} mol^{-1}$.

(2)

(v) Reaction **1** does not occur at room temperature due to its very high activation energy.

Suggest why the activation energy for Reaction **1** is very high.

(1)

....

....

....

(b) Magnesium silicide, Mg_2Si, reacts with hydrochloric acid forming silane, SiH_4, and magnesium chloride.

(i) Write an equation for this reaction.

State symbols are **not** required.

(1)

(ii) Silane has a molecular structure.

Complete the table, giving the shape of a molecule of SiH_4 and its bond angle.

(2)

Name of shape	
Bond angle	

(c) Silane spontaneously combusts in air at room temperature.

Reaction **2** $SiH_4(g) + 2O_2(g) \rightarrow SiO_2(s) + 2H_2O(l)$

Entropy data for this reaction are shown.

Species	$SiH_4(g)$	$O_2(g)$	$SiO_2(s)$	$H_2O(l)$
$S^\ominus$ / $J\,K^{-1}\,mol^{-1}$	204.5	205.0	41.8	69.9

(i) Calculate the entropy change of the system, ΔS_{system}, in $J\,K^{-1}\,mol^{-1}$, for Reaction **2**.

(2)

(ii) State why the entropy change of the surroundings for Reaction **2** is highly positive, in terms of the bond strengths of the reactants and products.

(1)

....

....

....

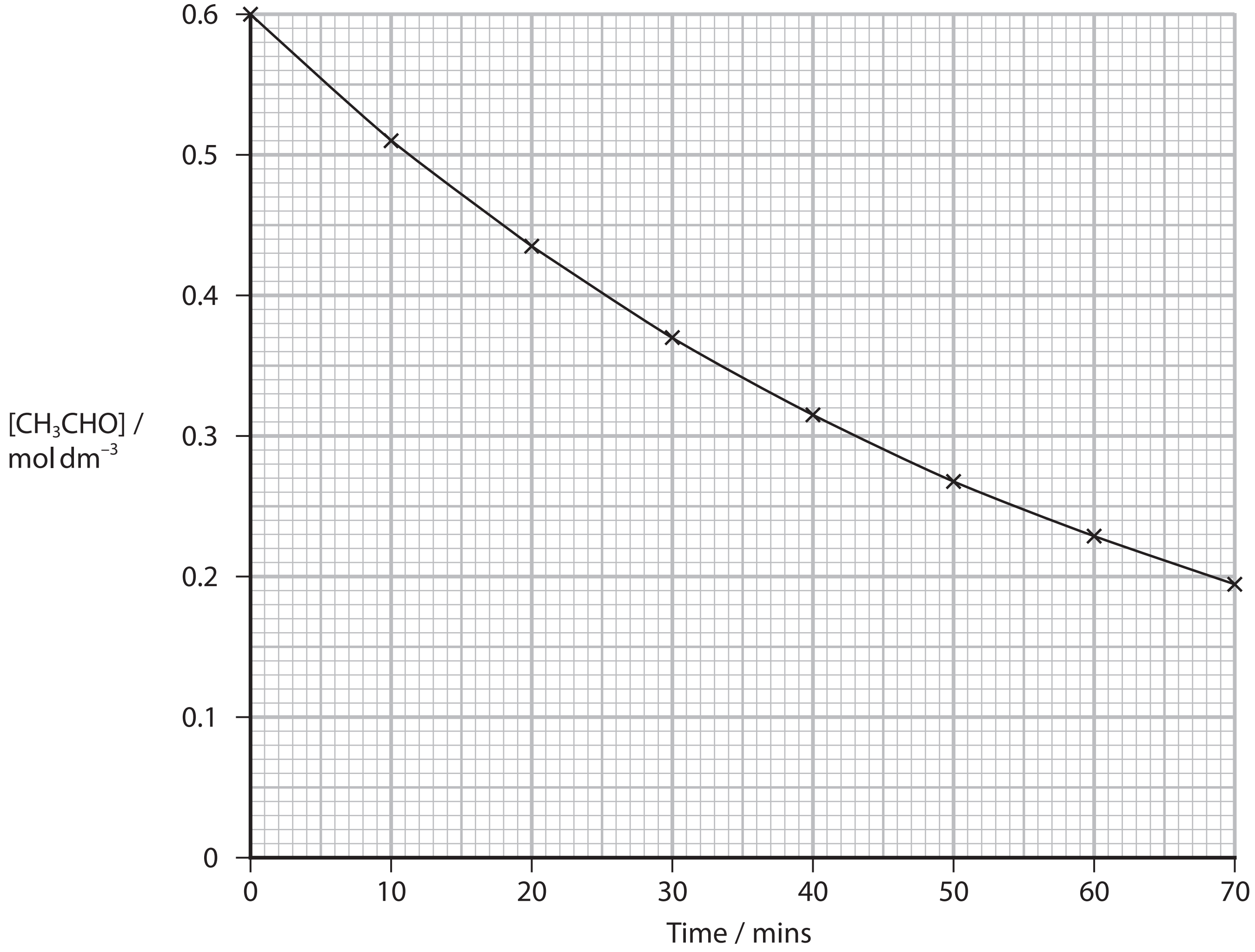
....

(Total for Question 15 = 15 marks)

16 This question is about the kinetics of the gas phase decomposition of CH_3CHO.

$$CH_3CHO \rightarrow CH_4 + CO$$

(a) A concentration-time graph for this reaction at 1000 K is shown.



(i) Calculate the initial rate of reaction, in **mol dm^{-3} s^{-1}**, at 1000 K.

You must show your working on the graph.

(3)

(ii) Deduce the rate equation for this reaction at 1000 K, by determining two half-lives.

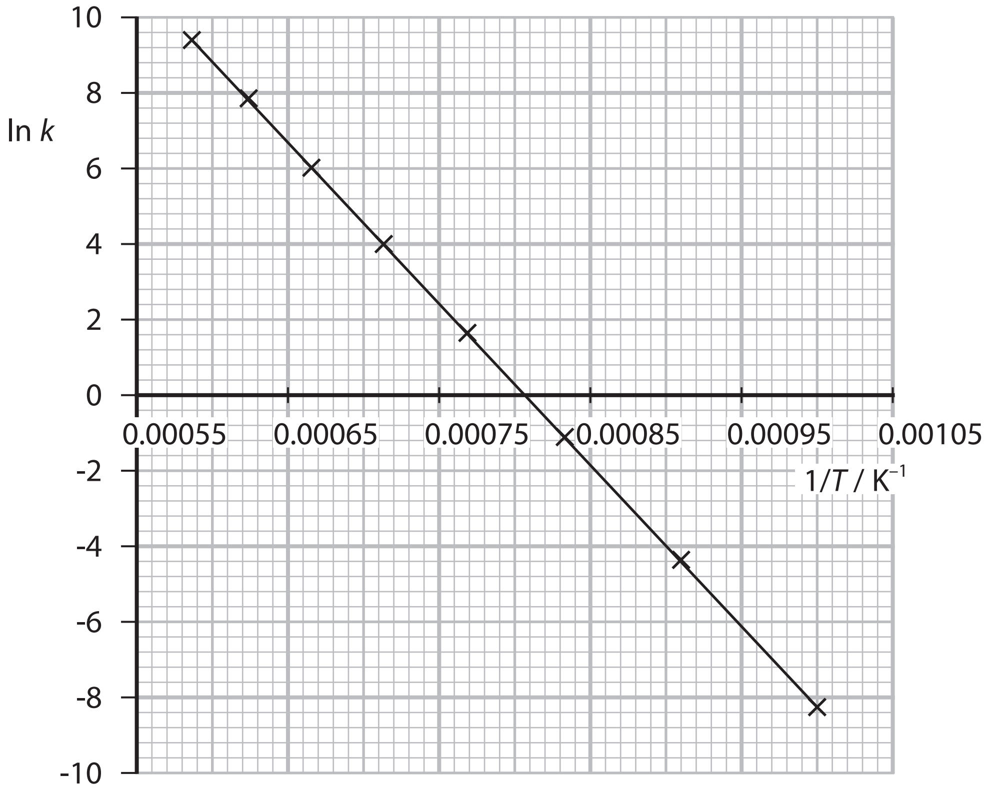
You must show your working on the graph.

(2)

....

(b) The rate constant, *k*, for the decomposition of CH_3CHO was determined between 1000 K and 1700 K.

The results are plotted on the graph of ln *k* against 1 / *T*.



Determine the activation energy, E_a, for this reaction.

Give your answer to **three** significant figures and include units.

$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \text{constant} \qquad R = 8.31\ \text{J mol}^{-1}\,\text{K}^{-1}$$

(4)

(Total for Question 16 = 9 marks)

Section B

Question Number	Answer	Additional Guidance	Mark
15(a)(i)	An answer that makes reference to the following points: • any one or two types of bonding **(1)** • third type of bonding **(1)**	Ignore giant throughout • covalent (in SiO_2) Ignore macromolecular Do not award simple/molecular Do not award dative/coordinate • metallic (in Mg) Allow metal • ionic (in MgO) Allow ion	**2**

Question Number	Answer	Additional Guidance	Mark
15(a)(ii)	An answer that makes reference to the following points: • (as) moles (decreases) from 5 to 3 **(1)** • decreases in disorder **(1)**	Accept reverse arguments Allow particles or molecules for moles Ignore any reference to standard entropies of reactants and products Allow just number of moles decreases Do not award incorrect numbers of moles Do not award incorrect explanation relating to states Accept fewer ways of distributing energy (in products) Accept fewer ways of arranging moles (in products) Ignore just less arranged for less disordered Ignore randomness for disorder Ignore just decreases in entropy	**2**

Question Number	Answer	Additional Guidance	Mark
15(a)(iii)	• expression for $\Delta S_{\text{surroundings}}$ **(1)** • value of $\Delta S_{\text{surroundings}}$ **(1)**	Example of calculation: $\Delta S_{\text{surroundings}} = \frac{-\Delta H}{T} = \frac{-(-370 \times 10^3)}{(23.0 + 273)}$ Allow just –(–370)/–(–370000)/370/370000 divided by any temperature in K or °C (+)1250 ($\text{J K}^{-1}\text{ mol}^{-1}$) Allow (+)1.25 $\text{kJ K}^{-1}\text{ mol}^{-1}$ Ignore SF except 1 SF Do not award any other answer Correct answer with some working scores (2) If neither mark awarded, –1250 ($\text{J K}^{-1}\text{ mol}^{-1}$) / –1.25 $\text{kJ K}^{-1}\text{ mol}^{-1}$ scores (1)	**2**

Question Number	Answer	Additional Guidance	Mark
15(a)(iv)	• expression for ΔS_{total} **(1)** • calculation of ΔS_{total} to 2, 3 or 4 SF **(1)**	Example of calculation: $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = -43.8$ + answer to (a)(iii) where answer to (a)(iii) is 1250 ($\text{J K}^{-1}\text{ mol}^{-1}$) ΔS_{total} = (+)1206 / 1210 / 1200 ($\text{J K}^{-1}\text{ mol}^{-1}$) Allow (+)1.206 / 1.21 / 1.2 $\text{kJ K}^{-1}\text{ mol}^{-1}$ where answer to (a)(iii) is –1250 ($\text{J K}^{-1}\text{ mol}^{-1}$) ΔS_{total} = –1294 / –1290 / –1300 ($\text{J K}^{-1}\text{ mol}^{-1}$) Allow –1.294 / –1.29 / –1.3 $\text{kJ K}^{-1}\text{ mol}^{-1}$ TE on transcription error of –48.3 for –43.8 No TE on incorrect expression from M1	**2**

Question Number	Answer	Additional Guidance	Mark
15(a)(v)	An answer that makes reference to the following point: - bonding / electrostatic attraction (in SiO_2) is strong **or** a large amount of energy is needed to break bond(s) (in SiO_2)	Ignore SiO_2/reaction/reactants is/are kinetically stable Ignore reactions between solids are slow Allow Mg/reactants for SiO_2 Allow a large amount of energy is needed to break covalent / metallic bond(s) Do not award any reference to the breaking of ionic bonds / intermolecular forces	**1**

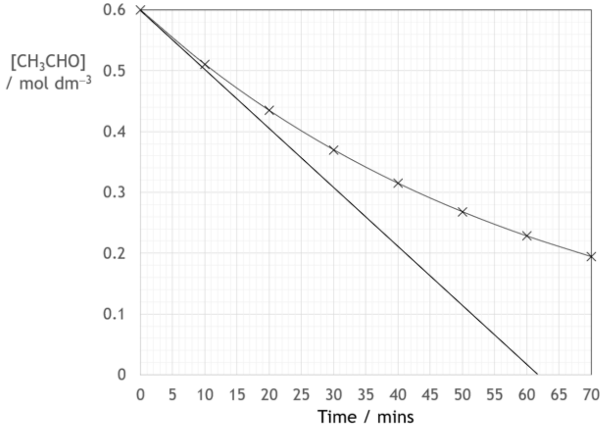
Question Number	Answer	Additional Guidance	Mark
15(b)(i)	An answer that makes reference to the following point: - correct equation	<u>Examples of equation:</u> $Mg_2Si + 4HCl \rightarrow SiH_4 + 2MgCl_2$ Allow ionic equations: $Mg_2Si + 4H^+ \rightarrow SiH_4 + 2Mg^{2+}$ $Mg_2Si + 4H^+ + 4Cl^- \rightarrow SiH_4 + 2Mg^{2+} + 4Cl^-$ Allow multiples Allow reversible arrow Ignore state symbols even if incorrect	**1**

Question Number	Answer		Additional Guidance	Mark
15(b)(ii)	An answer that makes reference to the following points:			**2**
	- name of shape	**(1)**	tetrahedral Allow tetrahedron	
	- bond angle	**(1)**	$109.5^{(\circ)}$ Allow $109^{(\circ)}$ No TE on incorrect shape	

Question Number	Answer		Additional Guidance	Mark
15(c)(i)			<u>Example of calculation:</u>	**2**
	- use of $\Delta S_{\text{system}} = \Sigma S^\ominus_{\text{products}} - \Sigma S^\ominus_{\text{reactants}}$	**(1)**	$\Delta S_{\text{system}} = (41.8 + 2 \times 69.9) - (204.5 + 2 \times 205.0)$ Allow just $\Delta S_{\text{system}} = \Sigma S^\ominus_{\text{products}} - \Sigma S^\ominus_{\text{reactants}}$	
	- calculation of ΔS_{system}	**(1)**	–432.9 TE on $\Delta S_{\text{system}} = \Sigma S^\ominus_{\text{reactants}} - \Sigma S^\ominus_{\text{products}}$ TE on incorrect numbers of moles and transcription errors Ignore units, even if incorrect Ignore SF except 1SF Correct answer with some working scores (2) +432.9 / –297.8 / +297.8 scores (1)	

Question Number	Answer	Additional Guidance	Mark
15(c)(ii)	An answer that makes reference to the following point: • O–H bonds are strong(er than Si–H bonds)	Accept reverse arguments Ignore $\Delta S_{\text{surroundings}}$ is (very) positive Ignore reaction is (highly) exothermic / ΔH is (very) negative Allow Si–O bonds are strong(er than Si–H bonds) Allow (covalent) bonding in H_2O / SiO_2 / products is strong Allow formation of product bonds releases more energy (than is required to break reactant bonds) Allow more energy required to break product bonds (than reactant bonds) Ignore any reference to O=O bond strength (which is greater than O–H / Si–O) Do not award intermolecular forces for bonds Do not award $\Delta S_{\text{surroundings}}$ is negative Do not award reaction is endothermic / ΔH is positive	**1**

(Total for Question 15 = 15 marks)

Question Number	Answer	Additional Guidance	Mark
16(a)(i)		<u>Example of calculation:</u> 	**3**
	- tangent drawn at $t = 0$ **(1)**		
	- calculation of gradient **of tangent** **(1)**	gradient = (-)0.6 ÷ 62 = (-)0.0096774 / (-)9.6774 × 10^{-3} Allow value in range of 0.0086 to 0.011 TE on any **tangent** Ignore sign and units Ignore SF except 1SF	
	- calculation of rate in mol dm^{-3} s^{-1} **(1)**	rate = (-)0.0096774 ÷ 60 = (-)0.00016129 / (-)1.6129 × 10^{-4} (mol dm^{-3} s^{-1}) Allow value in range of 0.00014 to 0.00019 / 1.4 × 10^{-4} to 1.9 × 10^{-4} TE on any concentration ÷ time value from M2 Ignore sign Ignore SF except 1SF Correct answer with tangent drawn at t = 0 scores (3) Correct answer with no tangent at t = 0 scores (2)	

Question Number	Answer	Additional Guidance	Mark
16(a)(ii)	An answer that makes reference to the following points: • working to show determination of two (or more) half-life values **(1)** • (constant half-life so first order and rate =) $k[CH_3CHO]^{(1)}$ **(1)**	eg, time for $[CH_3CHO]$ to fall from 0.6 to 0.3 = 43 – 0 = 43 eg, time for $[CH_3CHO]$ to fall from 0.4 to 0.2 = 68 – 25 = 43 Allow half-lives in range of 42 to 44 (mins) Allow half-lives in range of 2520 to 2640 (s) Accept working from either a statement in words or from working on the graph. Ignore 86 – 43 = 43 (mins) Ignore any attempt to find half-lives by extrapolation of the graph beyond 70 mins **Standalone mark** Do not award any other rate equation Do not award omission of *k*	**2**

Question Number	Answer	Additional Guidance	Mark
16(b)		<u>Example of calculation:</u>	**4**
	• calculation of gradient **(1)**	gradient = $\frac{(-8.2 - 9.4)}{(0.0010 - 0.000588)} = -42718$ (K) Allow value in range of –40500 to –44500 Ignore units Ignore SF except 1SF Do not award omission of negative sign	
	• use of $E_a = -\text{gradient} \times R$ **(1)**		
	• calculation of E_a **(1)**	$E_a = -(-42718) \times 8.31$ $= (+)354\,990$ TE on M1 TE on M2 for omission of negative sign only Accept use of 8.314 for 8.31 Ignore SF except 1SF Ignore units in M3	
	• calculated answer to 3SF **and** units **(1)**	(+)355 000 J mol^{-1} OR (+)355 kJ mol^{-1} TE on M3 Calculated final answer to 3SF with correct units in allowed range scores (4) gradient of –40500 gives 337 000 J mol^{-1} / 337 kJ mol^{-1} gradient of –44500 gives 370 000 J mol^{-1} / 370 kJ mol^{-1}	

(Total for Question 16 = 9 marks)

3 A group of students carried out an experiment to investigate the reaction between potassium manganate(VII) and ethanedioate ions in acid conditions.

The equation for the reaction is shown.

$$2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$$

Procedure

Step **1** Measure 10.0 cm^3 of potassium iodide solution into each of eight conical flasks.

Step **2** Measure 100.0 cm^3 of ethanedioic acid solution into a 250 cm^3 beaker. Add 25.0 cm^3 of potassium manganate(VII) solution and 5.0 cm^3 sulfuric acid to the beaker. Mix the contents of the beaker and start a timer.

Step **3** Immediately withdraw 10.0 cm^3 of reaction mixture and add it to the first conical flask containing (excess) potassium iodide solution.

Step **4** Continue removing 10.0 cm^3 of reaction mixture every minute for seven minutes. Each time, add the reaction mixture to a new conical flask containing the potassium iodide solution.

Step **5** Using starch as an indicator, titrate the iodine formed in the conical flasks with sodium thiosulfate solution.

The equation for the reaction in Step **3** is shown.

$$2MnO_4^-(aq) + 16H^+(aq) + 10I^-(aq) \rightarrow 2Mn^{2+}(aq) + 5I_2(aq) + 8H_2O(l)$$

The equation for the titration in Step **5** is shown.

$$2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

(a) (i) Explain why Step **3** effectively stops the reaction between potassium manganate(VII) and ethanedioate ions.

(2)

....

....

....

(ii) State when the starch indicator should be added during the titrations in Step **5**.

(1)

....

....

(b) A student's results are shown.

Time (t) / min	0	1	2	3	4	5	6	7
Volume of sodium thiosulfate / cm^3	30.00	29.80	28.60	27.50	19.00	7.50	2.50	1.50

(i) Plot a graph of volume of sodium thiosulfate against time.

(3)

(ii) Describe how the rate of reaction changes during the reaction.

(1)

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(iii) Explain why the rate of reaction changes in this way.

(3)

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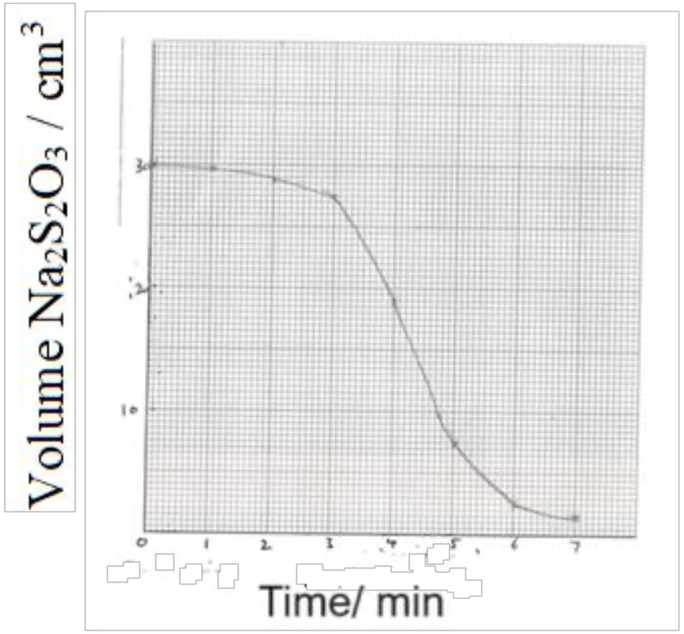
(Total for Question 3 = 10 marks)

Question Number	Answer		Additional Guidance	Mark
3(a)(i)	An answer that makes reference to the following points: • KI/I^-/iodide reacts with the MnO_4^- /manganate ((VII)) (rapidly) • MnO_4^- /manganate ((VII)) is **all** used up (so the reaction will stop)	(1) (1)	Allow the MnO_4^- gets reduced Allow the I^-/iodide gets oxidised by the MnO_4^- If oxidation numbers given, they must be correct Do not award the KI/I^-/iodide reacts with ethanedioate ions Allow so the MnO_4^- /manganate ((VII)) can no longer react (with the ethanedioate ions) Allow the manganate ((VII)) is the limiting reagent (with the KI) (so the reaction stops) KI/I^-/iodide reacts with **all** the MnO_4^- /manganate ((VII)) score 2 Ignore any reference to quenching	(2)

Question Number	Answer	Additional Guidance	Mark
3(a)(ii)	An answer that makes reference to the following point: • when the solution turns pale yellow/ straw coloured	Ignore towards the end of the titration Allow just yellow Allow yellow-brown Allow straw brown Do not award just brown/ pale brown/orange brown Do not award any reference to a ppt forming	(1)

Question Number	Answer	Additional Guidance	Mark
3(b)(i)	- suitable axes and labels with units Allow V/v/vol for volume **and** cm^3 $Na_2S_2O_3$ does not need to be seen Allow T/t for time **and** min The points plotted must cover at least half the grid in both directions **(1)** - points plotted correctly within one small square **(1)** - curved line of best fit **(1)** If graph is reversed penalise M1 only so max 2	Example of graph 	**(3)**

Question Number	**Answer**	**Additional Guidance**	**Mark**
3(b)(ii)	An answer that makes reference to the following point: • slow at the start, speeds up and then slows down	Allow just slow, fast, slow Allow low for slow Ignore any comment about the gradient and time	**(1)**

Question Number	**Answer**	**Additional Guidance**	**Mark**
3(b)(iii)	An answer that makes reference to the following points: • **Mn^{2+}** is a catalyst **(1)** • formed during the reaction (so the rate increases) **(1)** • reaction slows down as the reactants/ managanate ions/ethanedioate ions get used up **(1)**	 product is a catalyst / autocatalytic Do not award the reaction slows down as the catalyst/ thiosulfate/iodide gets used up.	**(3)**

(Total for Question 3 = 10 marks)

SECTION C

Answer ALL the questions. Write your answers in the spaces provided.

20 This question is about Group 2 compounds.

(a) Barium carbonate, $BaCO_3$, decomposes at high temperatures as shown.

$$BaCO_3(s) \rightarrow BaO(s) + CO_2(g)$$

(i) Calculate the standard entropy change for the system, $\Delta S^{\ominus}_{\text{system}}$.

Compound	Standard molar entropy / $J\,K^{-1}\,mol^{-1}$
$BaCO_3$	112.1
BaO	70.4
CO_2	213.6

(2)

(ii) The lowest temperature at which barium carbonate, $BaCO_3$, decomposes is 712 °C.

Use this information and your answer from (a)(i) to calculate the standard enthalpy change of the reaction, in $kJ\,mol^{-1}$.
Give your answer to an appropriate number of significant figures.

(3)

(b) Magnesium chloride, $MgCl_2(s)$, is used in the manufacture of tofu from soya milk.

An experiment was carried out to determine the enthalpy change of solution, $\Delta_{sol}H$, of anhydrous magnesium chloride, $MgCl_2(s)$.
4.26 g of anhydrous magnesium chloride was added to 200 cm^3 of deionised water in a polystyrene cup. The mixture was stirred to ensure all the solid dissolved to form a solution.
The temperature of the solution rose by 6.8 °C.

Calculate the enthalpy change of solution, $\Delta_{sol}H$, of anhydrous magnesium chloride, $MgCl_2(s)$.
Include a sign and units with your answer.

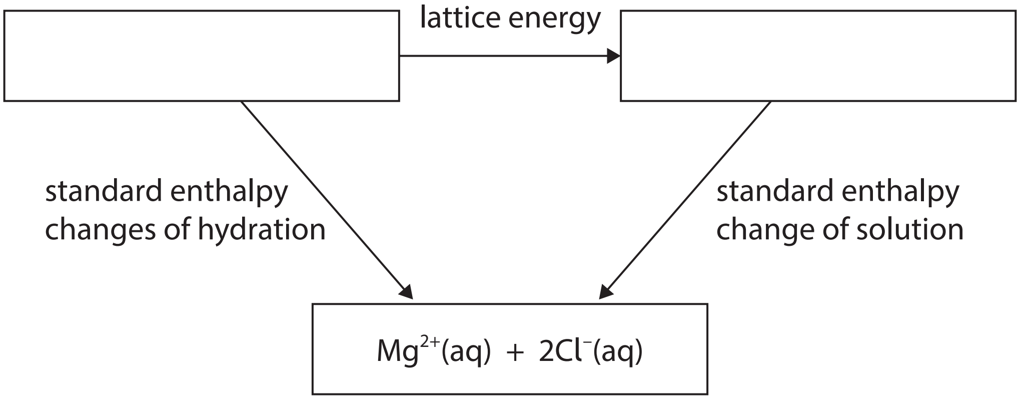
[Specific heat capacity of the solution = 4.18 $J\,g^{-1}\,°C^{-1}$]

(3)

(c) The standard enthalpy change of solution, $\Delta_{sol}H^{\ominus}$, of anhydrous $MgCl_2(s)$, can also be determined using a Hess Cycle.

(i) Complete the Hess Cycle shown by adding appropriate formulae, with state symbols, to the empty boxes.

(1)



[Lattice energy = –2526 $kJ\,mol^{-1}$
Standard enthalpy change of hydration of magnesium ions = –1920 $kJ\,mol^{-1}$]

(ii) Calculate the standard enthalpy change of hydration of chloride ions, $\Delta_{hyd}H^{\ominus}[Cl^{-}(g)]$, using the cycle and data in (c)(i) and your answer to (b).

[If you did not obtain a final answer to (b) use a value of $-155\,kJ\,mol^{-1}$. This is not the correct value.]

(3)

(d) The theoretical lattice energy for magnesium chloride, $MgCl_2(s)$, is $-2326\,kJ\,mol^{-1}$.

(i) Give **two** assumptions used in theoretical calculations of lattice energy.

(2)

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(ii) Explain the difference between the theoretical and experimental values for the lattice energy of magnesium chloride, $MgCl_2(s)$.

(3)

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(e) Hydrated barium chloride is a soluble, toxic salt. It can be formed from the reaction of barium carbonate with hydrochloric acid as shown.

$$BaCO_3 + 2HCl + nH_2O \rightarrow BaCl_2{\bullet}nH_2O + CO_2 + H_2O$$

A 5.00 g sample of barium carbonate reacted with 120 cm^3 of 0.500 $mol\,dm^{-3}$ hydrochloric acid.

(i) Show that the hydrochloric acid is in excess in this reaction.

(2)

(ii) All of the barium carbonate reacted and produced 6.19 g of hydrated barium chloride.

Calculate the relative formula mass of $BaCl_2 \bullet nH_2O$ and hence deduce the value of n.

(3)

(Total for Question 20 = 22 marks)

TOTAL FOR SECTION C = 22 MARKS
TOTAL FOR PAPER = 90 MARKS

Section C

Question Number	Answer	Additional Guidance	Mark
20(a)(i)	• expression for calculation of $\Delta S^{\theta}_{system}$ **(1)** • calculation of $\Delta S^{\theta}_{system}$ **(1)**	<u>Example of calculation</u> (70.4 + 213.6) − 112.1 = (+)171.9 (J K^{-1} mol^{-1}) Accept (+)172 (J K^{-1} mol^{-1}) Accept (+) 0.1719 kJ K^{-1} mol^{-1} If units are given for M2, they must be correct Allow 1 mark for final answer of − 171.9 (J K^{-1} mol^{-1}) Ignore SF except 1 SF Correct answer with no working scores (2) The only TE allowed from M1 to M2 is a transcription error in copying the data from the table	**(2)**

Question Number	Answer	Additional Guidance	Mark
20(a)(ii)	- recognition that at the minimum temperature for decomposition $\Delta S^{\theta}_{surr} = -\Delta S^{\theta}_{\text{system}}$ **(1)** - conversion of temperature to Kelvin **(1)** - calculation of ΔH **and** answer to **2 or 3 SF** **(1)** Alternative for M1 - recognition that at the minimum temperature for decomposition $\Delta G^{\theta} = 0$ OR $T = \Delta H \div \Delta S$	Example of calculation Allow TE from (a)(i) $\Delta S^{\theta}_{surr} = -171.9$ (J K^{-1} mol^{-1}) M1 can be subsumed within award of M3 712 + 273 = 985 (K) $\Delta H = -(985 \times -0.1719)$ = (+) 169.3 = (+) 169 / 170 (kJ mol^{-1}) Allow $\Delta H = -(985 \times -171.9)$ = (+) 169300 = 169000 / 170000 J mol^{-1} Allow TE from M1 to M3 Correct answer with no working scores 3	**(3)**

Question Number	Answer	Additional Guidance	Mark
20(b)	- calculation of energy released **(1)** - calculation of moles of anhydrous magnesium chloride **(1)** - calculation of $\Delta_{sol}H$, including sign and unit **(1)**	Example of calculation Allow TE throughout $4.18 \times 200 \times 6.8 = 5684.8$ (J) Ignore any signs in M1 Do not award use of mass = 204.26 $4.26 \div 95.3 = 0.044701$ (mol) $5684.8 \div 0.044701 = 127170$ J mol^{-1} so $\Delta_{sol}H = -127$ kJ mol^{-1} / -127170 J mol^{-1} Correct answer with no working scores 3 Ignore SF except 1 SF	**(3)**

Question Number	Answer	Additional Guidance	Mark
20(c)(i)	An answer that makes reference to the following points: • correct formulae and state symbols in left hand box **and** correct formula and state symbol in right hand box	$Mg^{2+}(g) + 2Cl^{-}(g)$ $MgCl_2(s)$	**(1)**

Question Number	Answer	Additional Guidance	Mark
20(c)(ii)	• expression for standard enthalpy of hydration **(1)** • calculation of enthalpy of hydration of chloride ions **(1)** • calculation of standard enthalpy of hydration of chloride ions **(1)**	Example of calculation $-2526 + (-127) = -1920 + 2\Delta_{hyd}H[Cl^-(g)]$ $2\Delta_{hyd}H[Cl^-(g)] = [-2526 + (-127)] + 1920$ $= -733$ (kJ mol^{-1}) $-733 \div 2 = -366.5 / -367$ (kJ mol^{-1}) OR $-2526 + (-155) = -1920 + 2\Delta_{hyd}H[Cl^-(g)]$ $2\Delta_{hyd}H[Cl^-(g)] = [-2526 + (-155)] + 1920$ $= -761$ (kJ mol^{-1}) $(= -761 \div 2) = -380.5 / -381$ (kJ mol^{-1}) Allow TE from b for M1 No TE from M1 into M2 for incorrect expression, apart from transcription error from b, or value carried though from (b) with incorrect units Allow TE from M2 to M3 Correct answer with no/some working scores (3) Ignore SF except 1 SF Allow use of − 155 even if an answer is evaluated in (b)	**(3)**

Question Number	Answer	Additional Guidance	Mark
20(d)(i)	An answer that makes reference to two of the following points:		**(2)**
	- the bonding is 100% ionic / the bonding is **only** ionic **(1)**	Allow no covalent character Allow 'it is 100% ionic'	
	- the ions are in contact with each other **(1)**		
	- the ions are perfect spheres **(1)**	Allow no distortion of electron cloud of Cl^- / chloride ion Allow no polarisation of Cl^- / chloride ion Ignore polarisation of chlor**ine**	
	- the charges are point charges **(1)**	Allow the charge is distributed evenly across the ions	

Question Number	Answer	Additional Guidance	Mark
20(d)(ii)	An explanation that makes reference to the following points:	Allow reverse argument for M1 and M3	**(3)**
	- experimental value is more exothermic **(1)**	Allow more negative Allow greater in magnitude Ignore experimental value is larger / smaller	
	- (because the) chloride ion is polarised (by the magnesium ion) **(1)**		
	- giving (the bonding in) magnesium chloride some covalent character (so the bonding is stronger) **(1)**		

Question Number	Answer	Additional Guidance	Mark
20(e)(i)	- calculation of moles of $BaCO_3$ **and** HCl **(1)** - show that number of moles of $BaCO_3$ is less than that required to react with moles of HCl **(1)**	Example of calculation 5.00 ÷ 197.3 = 0.025342 (mol) **and** (120 ÷ 1000) × 0.5 = 0.06 (mol) Both correct answers with no working scores (1) Allow use of 137 for A_r of Ba 0.02534 < (0.06 ÷ 2) / 0.02534 < 0.03 Allow reverse argument i.e. HCl (0.06) is > 2 × $BaCO_3$ (0.05068) Allow TE from M1 only if it shows HCl in excess	**(2)**

Question Number	Answer	Additional Guidance	Mark
20(e)(ii)		Example of calculation	**(3)**
	- calculation of moles of $BaCO_3$ (= moles of $BaCl_2$) **and** calculation of relative formula mass of $BaCl_2•nH_2O$ **(1)**	(5.00 ÷ 197.3 =) 0.02534 (mol) 6.19 ÷ 0.02534 = 244.26 (g mol^{-1})	
	- calculation of formula mass due to nH_2O **(1)**	244.26 − (137.3 + 71) = 35.96	
	- calculation of n to nearest whole number **(1)**	(35.96 ÷ 18 = 1.9978) = 2	
		Correct final answer with no working scores M3 only	
	Alternative method		
	- deduction of moles of anhydrous $BaCl_2$ **and** calculation of mass of anhydrous $BaCl_2$ **(1)**	0.02534 × (137.3 + 71) = 5.2788 (g)	
	- calculation of mass of water of crystallisation **(1)**	6.19 − 5.2788 = 0.9112 (g)	
	- calculation of mole of water of crystallisation **and** n to nearest whole number **(1)**	0.9122 ÷ 18 = 0.05062 0.05062 ÷ 0.02534 = 1.9977 = 2	

(Total for Question 20 = 22 marks)
TOTAL FOR SECTION C = 22 MARKS
TOTAL FOR PAPER = 90 MARKS

2 A group of students investigated the kinetics of the reduction of peroxydisulfate ions by iodide ions in aqueous solution, as shown in Reaction **1**.

Reaction **1** $S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$

Some of the iodine produced in Reaction **1** may be removed by including a portion of sodium thiosulfate in the reaction mixture.
The thiosulfate ions react with the iodine as shown in Reaction **2**.

Reaction **2** $2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$

After all the thiosulfate ions have reacted, any further iodine produced can be detected by the formation of a starch-iodine complex. Student **M** carried out a sequence of experiments to determine the order of the reaction with respect to **iodide ions**.

The volumes of the solutions used in the mixtures are shown in Table **1**.

Table **1**

Mixture	Volume KI(aq) / cm^3	Volume $K_2S_2O_8$(aq) / cm^3	Volume $Na_2S_2O_3$(aq) / cm^3	Volume H_2O(l) / cm^3
1	18.0	20.0	5.0	2.0
2	15.0	20.0	5.0	5.0
3	11.0	20.0	5.0	9.0
4	7.5	20.0	5.0	12.5
5	4.0	20.0	5.0	16.0

The concentrations of the solutions used were

Potassium iodide	KI(aq)	0.200 mol dm^{-3}
Potassium peroxydisulfate	$K_2S_2O_8$(aq)	0.100 mol dm^{-3}
Sodium thiosulfate	$Na_2S_2O_3$(aq)	0.00500 mol dm^{-3}

Procedure

Step **1** A few drops of starch solution are added to 5.0 cm^3 sodium thiosulfate solution in a small beaker.

Step **2** The potassium peroxydisulfate solution and water are added to the beaker.

Step **3** Then potassium iodide solution is added, the mixture stirred and a timer is started. The time taken to change colour is recorded.
The procedure is repeated for each mixture using the volumes shown in Table **1**.

(a) (i) Suggest a suitable piece of apparatus for measuring the volume of the potassium iodide solution.

(1)

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(ii) State the final colour of the reaction mixture in Step **3**.

(1)

....

(iii) The reciprocal of the time taken for the mixture to change colour (1 / time), can be used as an approximate measure of the initial rate.

State why the amount of added thiosulfate ions should be much smaller than the amount of peroxydisulfate or iodide ions for this approximation to be valid.

(1)

....

....

....

(iv) State why is it important that the rate of Reaction **2** is much faster than that of Reaction **1**.

(1)

....

....

(b) The results that Student **M** obtained are shown.

Table **2**

Mixture	$[I^-]$ / mol dm^{-3}	time / s	1 / time / s^{-1}
1	0.080	130	0.0077
2	0.067	157	0.0064
3		202	0.0050
4	0.033	320	0.0031
5	0.018	658	0.0015

(i) Complete Table **2** with the iodide ion concentration in Mixture 3, using the information from Table **1** and the concentration of the potassium iodide solution.

(1)

(ii) Plot a graph of 1 / time against the iodide ion concentration.

(2)

(iii) Deduce the order of the reaction with respect to iodide ions.

Justify your answer.

(2)

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(c) (i) Student **N** carried out a sequence of experiments to find the order of reaction with respect to **peroxydisulfate ions**, using solutions of the same concentration.

The volumes of potassium peroxydisulfate solution used were different.

State **two** variables which should be kept the same.

(2)

....

....

(ii) Student **N** found that the reaction is first order with respect to peroxydisulfate ions.

Write the overall rate equation for the reaction of peroxydisulfate ions with iodide ions.

(1)

(d) Student **R** carried out experiments to find the activation energy of this reaction. A similar procedure was used to determine the rate of reaction at two different temperatures.

The results of these experiments are shown.

T / °C	T / K	$1/T$ / K^{-1}	t / s	k / dm^3 mol^{-1} s^{-1}	ln k
12	285	0.00351	265	2.4×10^{-3}	–6.03
45	318	0.00314	20	3.1×10^{-2}	–3.47

Calculate, without drawing a graph, the activation energy of the reaction.

You should include a sign and units in your answer.

$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \text{constant} \qquad R = 8.31\ \text{J K}^{-1}\,\text{mol}^{-1}$$

(3)

(Total for Question 2 = 15 marks)

Question Number	Answer	Additional Guidance	Mark
1(b)	An answer that makes reference to the following points: • iodine has been produced (from iodide ions) **(1)** • Fe(III) is reduced /Iron is reduced from +3 to +2 **(1)** **or** I^- oxidised/iodine is oxidised from -1 to 0	Allow I^- changes to I_2 Iodide ions oxidised to iodine scores both marks Allow Fe(III) acts as an oxidising agent/I^- acts as reducing agent Ignore references to the identity of the white ppt Do not award unbalanced (half)equations for M2	**(2)**

(Total for Question 1 = 9 marks)

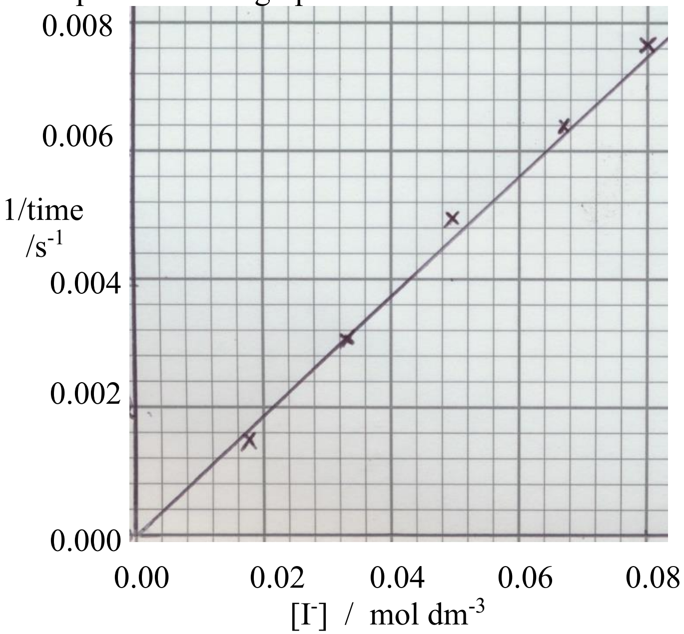
Question Number	Answer	Additional Guidance	Mark
2(a)(i)	An answer that makes reference to the following point: • burette or graduated pipette or pipettes with markings	Do not award just pipette Do not award volumetric pipette/flask Do not award measuring cylinder	**(1)**

Question Number	Answer	Additional Guidance	Mark
2(a)(ii)	An answer that makes reference to the following point: • blue/black/blue-black/dark blue	Allow colourless to blue/black Allow black-blue Do not award colourless/yellow/brown/purple	**(1)**

Question Number	Answer	Additional Guidance	Mark
2(a)(iii)	An answer that makes reference to the following point: • the rate of reaction does not change significantly/is constant at the start of the reaction	Allow (so that)any change in concentration of the peroxydisulfate/iodide does not affect the reaction rate Allow so that the thiosulfate ions are used up/ Reaction 2 is complete before the concentrations of the reactants changes (significantly) Allow so that the concentration of the reactants does not change(significantly) Ignore any references to the rate depending on the thiosulfate concentration Ignore references to the iodine/iodide being completely used up	**(1)**

Question Number	Answer	Additional Guidance	Mark
2(a)(iv)	An answer that makes reference to the following point: • so that the iodine disappears (in the reaction with the thiosulfate) before any reaction with the starch can occur	Allow arguments based on a slower rate for Reaction **2** e.g. the iodine would not be removed / the colour (of the complex) would appear too soon / straightaway/the colour change is delayed/not all the thiosulfate will react	**(1)**

Question Number	Answer	Additional Guidance	Mark
2(b)(i)	• concentration potassium iodide in mixture **(1)**	Example of calculation $11 \times 0.200 \div 45 = 0.049$ (mol dm^{-3}) Ignore SF except 1 SF	**(1)**

Question Number	Answer	Additional Guidance	Mark
2(b)(ii)	An answer that makes reference to the following points: • axes, labels with units **and** scale chosen to cover at least half the graph in each direction **(1)** • 1st two and last two points correctly plotted (allow one small square) and best fit straight line. Ignore third point. **(1)**	Example of correct graph  Allow axes reversed	**(2)**

Question Number	Answer	Additional Guidance	Mark
2(b)(iii)	An explanation that makes reference to the following points: • first order **(1)** • since the graph (of rate against concentration) is a straight line (through the origin)/ the rate/1/t is proportional to the concentration of iodide ions **(1)**	M2 is dependent on M1 Allow the gradient is constant Ignore references to half-lives Do not award contradictory reasoning e.g. concentration is proportional to time	**(2)**

Question Number	Answer	Additional Guidance	Mark
2(c)(i)	An explanation that makes reference to two of the following points: • the temperature **(1)** • the (total) volume of the reaction mixture **(1)** • the volume of the KI (solution)/iodide ions **(1)** • the volume of $Na_2S_2O_3$ (solution)/thiosulfate **(1)**	Accept just “total volume” Allow the volumes of other reactants for 1 mark Ignore references to concentration of individual reactants. Do not award the volume of peroxydisulfate Do not award pressure	**(2)**

Question Number	Answer	Additional Guidance	Mark
2(c)(ii)	An answer that makes reference to the following point: • rate = $k[S_2O_8^{2-}]\,[I^-]$	Allow $[I^-]\,[S_2O_8^{2-}]$ Allow K	**(1)**

Question Number	Answer	Additional Guidance	Mark
2(d)	• two simultaneous equations **(1)**	$-6.03 = -(E_a \times 0.00351 \div R) + \text{constant}$ $-3.47 = -(E_a \times 0.00314 \div R) + \text{constant}$	**(3)**
	• subtraction **(1)**	$-2.56 = -(E_a \times 0.00037 \div R)$	
	• evaluation of activation energy with sign and units **(1)**	(+)57.496 kJ mol^{-1} / (+)57496/57500/57000 J mol^{-1} Ignore SF except 1 SF Correct answer with some evidence of working scores 3 Using values correctly rounded to 3SF (+)58181/58180/ 58200/58000 J mol^{-1} Using 1/285 and 1/318 gives (+)58425/58430/58400/58000 J mol^{-1}	
	An alternative method: • in a graph of lnk against 1/T the gradient gives −Ea/R • gradient can be found by subtraction of lnk ÷ subtraction of 1/T	gradient = $\frac{-3.47 - (-6.03)}{0.00314 - 0.00351} = -6918.9\ \text{K}^{-1}$	
	• rearrangement to give Ea	$-(-6918.9 \times 8.31) = (+)\ 57.496$ kJ mol^{-1} Ignore SF except 1 SF	

(Total for Question 2 = 15 marks)

(b) An initial-rates method may be used to investigate the kinetics of the reaction between hydrogen peroxide and iodide ions in acid solution.
The equation for this reaction is shown.

$$H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow I_2(aq) + 2H_2O(l)$$

The reaction mixture contains a small amount of thiosulfate ions which reduce the iodine back to iodide ions.
The equation for this reduction is shown.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

As soon as the thiosulfate is used up, the iodine that is further produced reacts with the starch present and results in a colour change. The time taken for this colour change is noted and the reciprocal of this time is used as a measure of reaction rate.

The results from a series of experiments where the volume of the hydrogen peroxide was changed are given in the table.

Reaction rate / s^{-1}	0.9×10^{-2}	1.8×10^{-2}	2.5×10^{-2}	3.7×10^{-2}	4.6×10^{-2}
Volume of H_2O_2 / cm^3	10	20	30	40	50

(i) Give the colour **change** after all the thiosulfate is used up.

(2)

....

(ii) Plot a graph of reaction rate against volume of hydrogen peroxide.

(3)

(iii) State and justify the reaction order with respect to hydrogen peroxide by using your graph.

(1)

....

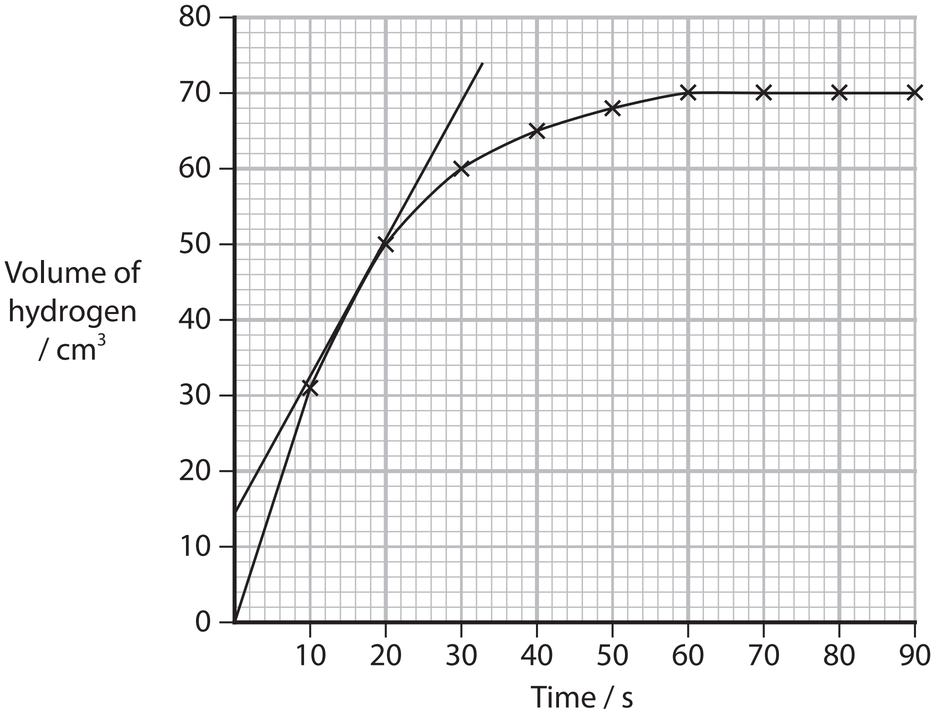
....

....

(c) The continuous monitoring method was used to investigate the kinetics of the reaction between magnesium and sulfuric acid at different temperatures. The equation for the reaction is shown.

$$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$$

(i) The graph shows the results of an experiment at 80°C.



Calculate the reaction rate at 15 seconds using the tangent shown.

Give your answer to two significant figures and include units, if any.

(2)

(ii) The temperature of the reaction was changed to 75°C.
Draw a line on the graph to show the possible results if this was the only change. Justify any similarities and differences in the lines.

(2)

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(Total for Question 18 = 16 marks)

19 Many effervescent products such as vitamin tablets are solids which contain citric acid, $C_6H_8O_7$, and sodium hydrogencarbonate. Only when these tablets are added to water is fizzing observed. The equation for the reaction is shown.

$$C_6H_8O_7 + 3NaHCO_3 \rightarrow 3H_2O + 3CO_2 + Na_3C_6H_5O_7$$

(a) Give **two** reasons why this reaction is thermodynamically feasible when considering the entropy of the system.

(2)

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....

....

(b) Describe, in terms of the particles involved, why the reaction does not occur until the tablets are dissolved in water.

(3)

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(c) For the reaction at 25°C, the standard entropy change of the surroundings, $\Delta S^{\ominus}_{\text{surroundings}} = -234.9\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$.

Calculate the enthalpy change of the reaction.
Include a sign and units in your answer.

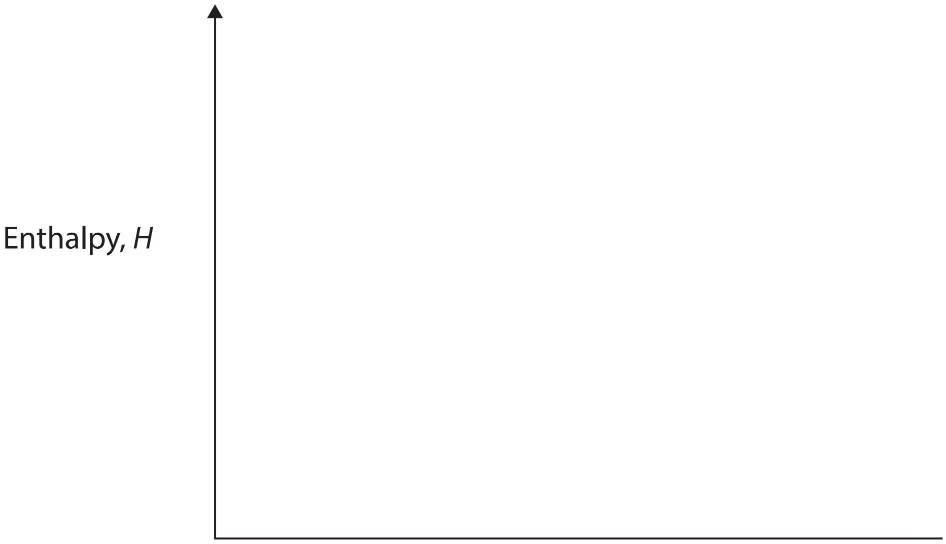
(2)

(d) The enthalpy change of solution, $\Delta_{sol}H$, of sodium hydrogencarbonate is $+18.6\,kJ\,mol^{-1}$.

Sketch the enthalpy level diagram to show the relationship between the enthalpy change of solution, lattice energy and enthalpies of hydration for the dissolving of sodium hydrogencarbonate in water.

Fully label your diagram.

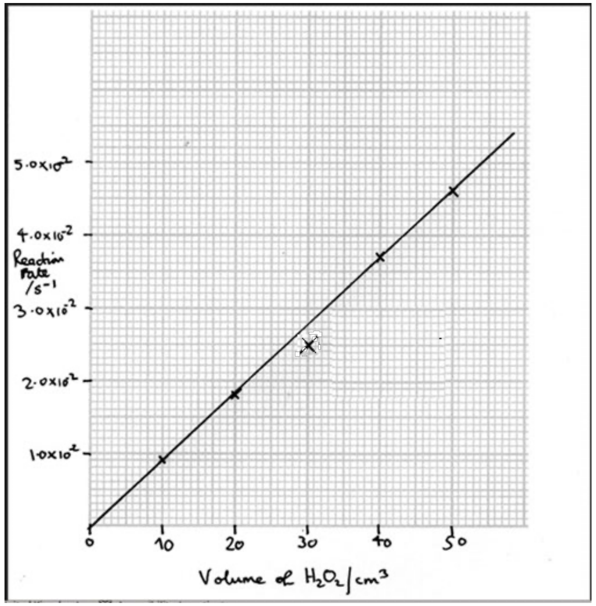
(3)



(Total for Question 19 = 10 marks)

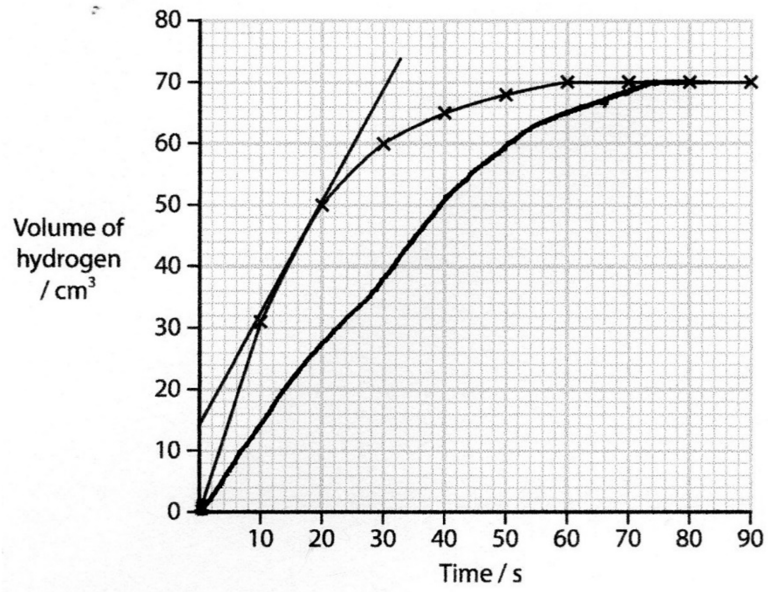
TOTAL FOR SECTION B = 49 MARKS

Question Number	**Answer**	**Additional Guidance**	**Mark**
18(b)(i)	An answer that makes reference to the following point • from colourless **(1)** • to blue-black/blue/black **(1)**	Do not award clear Do not award if any colour is given Standalone mark Ignore shades Allow (1) for reversed answer i.e. black to colourless	**(2)**

Question Number	Answer	Additional Guidance	Mark
18(b)(ii)	- labelled axes with units **(1)** - plotting of points and straight line (±½ square) **(1)** - scale to ensure points cover over half the graph paper **(1)**	Allow just 'rate' and just 'volume' with appropriate units Allow V(H_2O_2) for volume Allow small dots for plotted crosses Ignore absence of line to the origin Example of graph 	**(3)**

Question Number	Answer	Additional Guidance	Mark
18(b)(iii)	An answer that makes reference to the following point - first order/ one/ 1 **and** straight-line graph (passing through origin)	Allow rate is (directly) proportional volume (of H_2O_2) Allow rate doubles when volume doubles Allow graph has constant (positive) gradient Do not award if there is no graphical line No TE from incorrect graph	**(1)**

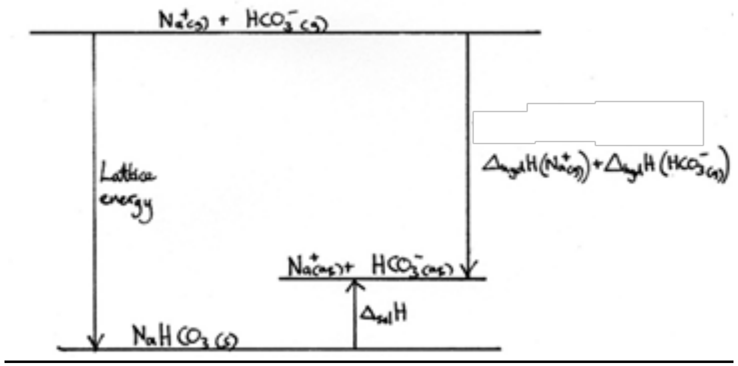
Question Number	Answer	Additional Guidance	Mark
18(c)(i)	- reaction rate value to 2 SF **(1)** - units **(1)**	<u>Example of calculation</u> rate = (72 – 18) ÷ (32 − 2) = 1.8 Allow 1.9 $cm^3\ s^{-1}$ Allow cm^3 / s Standalone mark	**(2)**

Question Number	Answer	Additional Guidance	Mark
18(c)(ii)	An answer that makes reference to the following points: • line on the graph which is below the current line **and** (lower temperature means a) slower reaction rate **(1)** • plateaus at 70 cm^3 **and** concentration remains the same **(1)**	Allow ends at 70 for plateaus Allow reference to temperature not changing the yield Allow (1) for a correct line without justification / with incorrect justification if no other mark awarded Allow description of line and justification for either M1 or M2 but not both marks if no line drawn Exemplar graph 	**(2)**

Question Number	Answer	Additional Guidance	Mark
19(a)	An answer that makes reference to the following points: • a gas (and liquid products) are produced (from solids) **(1)** • more moles of products than reactants / increase in moles **(1)**	Ignore just carbon dioxide produced Ignore just change of state Do not award reference to two gases/H_2O gas Accept moles increase from 4 to 7 Allow reference to molecules / particles Do not award if numbers of moles incorrect Ignore references to exothermic / endothermic	**(2)**

Question Number	Answer	Additional Guidance	Mark
19(b)	An explanation that makes reference to the following points: • in solids the particles are fixed / in a lattice (so unable to move) **(1)** • so they cannot collide and react **(1)** • but when dissolved in water the particles are mobile **(1)**	Allow M2 if applied to the dissolved ions being able to collide and react Do not award reference to an increase in kinetic energy Allow when dissolved the ions are dissociated / spread out (in solution) Ignore references to entropy / energy changes / activation energy	**(3)**

Question Number	Answer	Additional Guidance	Mark
19(c)	• calculation of enthalpy change value **(1)** • sign **and** units **(1)**	Example of calculation $\Delta H = (-\Delta S_{\text{surroundings}} \times T = --234.9 \times 298 =)$ $\Delta H = +70000.2 / 70000 / 7.0 \times 10^4$ J mol^{-1} or $\Delta H = +70.002 / 70 / 7.0 \times 10^1$ kJ mol^{-1} Ignore SF Allow J / mol or kJ / mol for units If two answers are given then both must be correct Correct answer without working scores (2) Allow M2 for incorrect value provided the units match the value, e.g. use of 25 instead of 298 gives +5872.5 J mol^{-1} or 5.8725 kJ mol^{-1}	**(2)**

Question Number	Answer	Additional Guidance	Mark
19(d)	• enthalpy of solution labelled arrow shown to go up from solid $NaHCO_3$ **(1)** • lattice energy gaseous species and labelled arrow to go down **(1)** • enthalpy of hydration labelled arrow to go down and both aqueous ions species **(1)**	Example of sketch  Accept two labelled arrows if the hydration enthalpies for the ions are written separately Allow just singular $\Delta_{hyd}H$ for hydration enthalpy of both ions Accept +18.6 for $\Delta_{sol}H$ Allow ΔH_{hyd} for $\Delta_{hyd}H$ and ΔH_{sol} for $\Delta_{sol}H$ Allow any lengths of arrows	**(3)**

4 Phenolphthalein is an indicator used in acid-base titrations. It can be represented by the simplified formula H_2In. When mixed with an excess of hydroxide ions it reacts rapidly, forming a pink solution, due to the ion In^{2-}.

The pink colour then fades as the colourless ion $InOH^{3-}$ forms.

$$\underset{\text{pink}}{In^{2-}(aq)} + OH^{-}(aq) \rightarrow \underset{\text{colourless}}{InOH^{3-}(aq)}$$

(a) A student carried out an experiment to find the order of this reaction with respect to In^{2-}.

A solution of phenolphthalein was mixed with a large excess of potassium hydroxide solution.
The resulting solution contains In^{2-} of concentration 0.00500 mol dm^{-3}.

The concentration of In^{2-} was measured over a time period of 300 seconds.

Time /s	Concentration of In^{2-} / mol dm^{-3}
0	0.00500
30	0.00380
60	0.00280
120	0.00150
150	0.00110
210	0.00060
270	0.00030
300	0.00020

(i) Give the name of the most suitable technique to monitor the concentration of In^{2-} during the reaction.

(1)

....

....

(ii) Plot a graph of the concentration of In^{2-} against time.

(3)

(iii) Determine **two** successive half-lives for the concentration of In^{2-}.
You must show your working on the graph.

(2)

First half-life ....

Second half-life ....

(iv) Deduce the order with respect to In^{2-}.

Justify your answer.

(2)

....

....

....

....

....

(v) Explain why the results of this experiment do not allow the overall order of the reaction to be determined.

(2)

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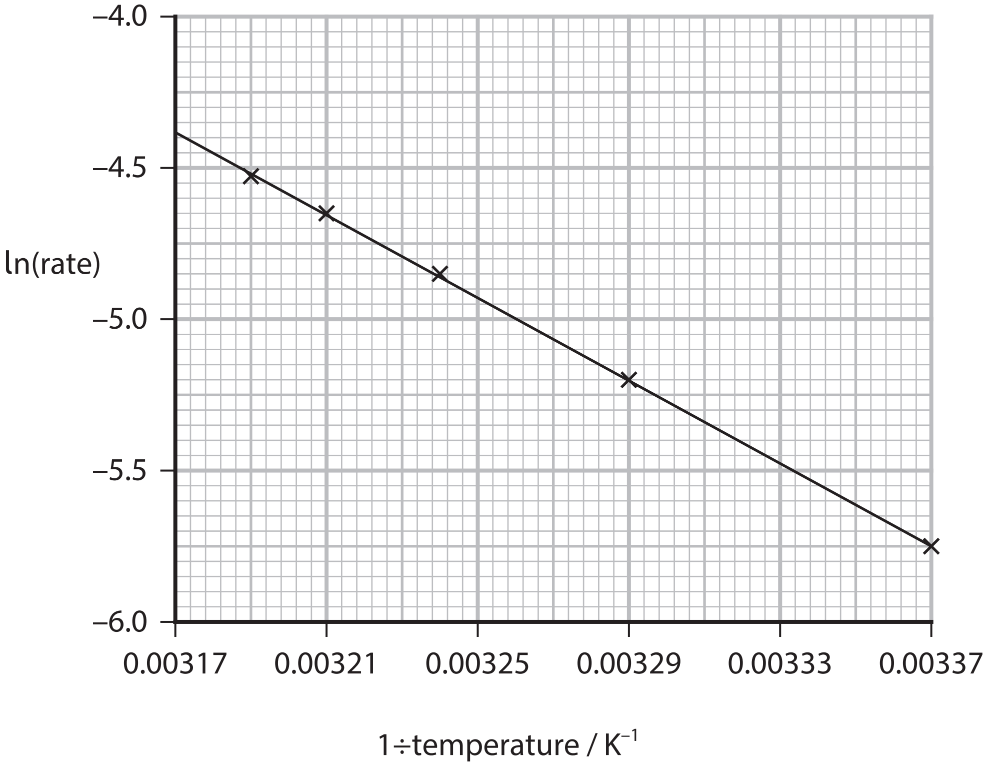
(b) Another student carried out an experiment to find the activation energy of the reaction between In^{2-} and hydroxide ions.

A graph of ln(rate) against 1÷temperature was plotted using the data obtained.



(i) Calculate the activation energy for the reaction, using the gradient of the graph and the Arrhenius equation shown.

Give your answer to an appropriate number of significant figures, including a sign and units.

$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \ln(\text{collision factor}) \qquad R = 8.31\,\text{J mol}^{-1}\,\text{K}^{-1}$$

(3)

(ii) A value for ln(collision factor) of –4.4, given to two significant figures, was suggested by the student.

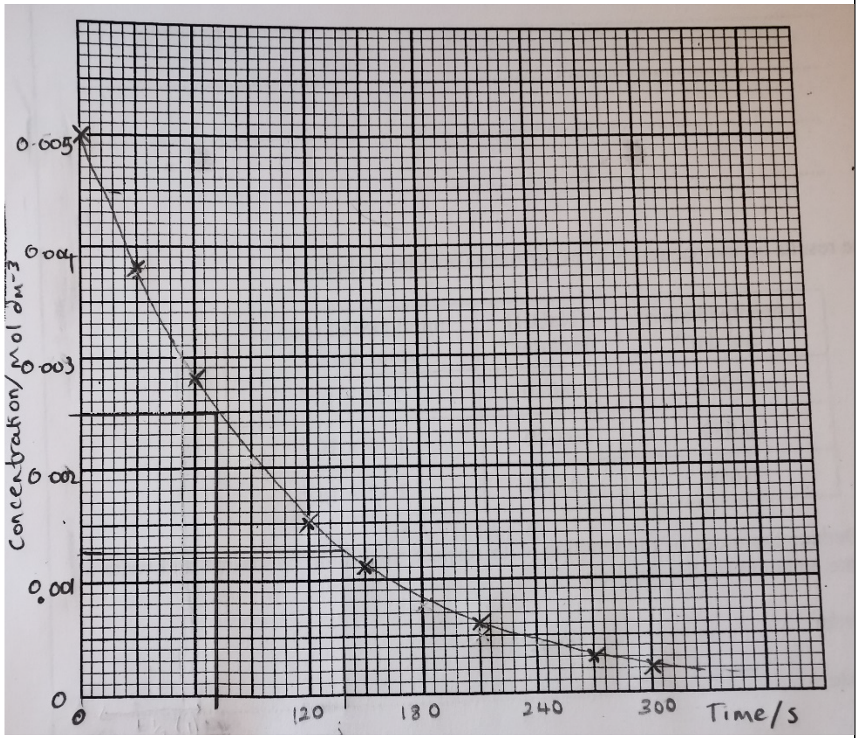
State whether or not you agree with this value. Justify your answer.

(1)

(Total for Question 4 = 14 marks)

TOTAL FOR PAPER = 50 MARKS

Question Number	Answer	Additional Guidance	Mark
4(a)(i)	• colorimetry	Allow colorimeter Ignore light detector Comment If second incorrect technique shown and not crossed out then DNA	**(1)**

Question Number	Answer	Additional Guidance	Mark
4(a)(ii)	• axes labelled with units, with time on x axis, concentration (of In^{2-}) on y axis **(1)** • suitable scale where points plotted cover at least half the available space **(1)** • all points plotted within ±½ a small square **and** smooth curve drawn **(1)**	Example of graph  Allow t/s Do not award T/s	**(3)**

Question Number	Answer	Additional Guidance	Mark
4(a)(iii)	• first half-life determined **(1)** • second half-life determined, consecutive with first **(1)** Comment if 2 half-lives given are within range but there is no evidence of working on the graph allow 1 mark max	Example of calculation 72 (s) 138 − 72 = 66 (s) Accept two values between 60 and 75 Allow two half-lives that are not successive Allow half-lives shown in (iv)	**(2)**

Question Number	Answer	Additional Guidance	Mark
4(a)(iv)	An answer that makes reference to the following points: • first order (with respect to In^{2-}) **(1)** • as (successive) half-lives are (approximately) constant **(1)**	M1 is standalone regardless of half-lives in (iii) M2 is dependent on similar /constant half lives in (iii) Comment If 2nd half life is incorrectly calculated to be approximately double that of the first half life, allow 1 mark for 2nd order, as half-lives double / are not constant	**(2)**

Question Number	Answer	Additional Guidance	Mark
4(a)(v)	An explanation that makes reference to the following points: EITHER • as hydroxide (ions) are in (large) excess **(1)** • so as hydroxide ions react the change in their concentration is negligible / their concentration remains constant (so does not affect the rate) **(1)** OR (to find the overall order) • carry out another experiment where [OH^-] changes **(1)** • and [In^{2-}] is kept constant **(1)**	Allow KOH / NaOH is in (large) excess Ignore references to limiting factor	**(2)**

Question Number	Answer	Additional Guidance	Mark
4(b)(i)		<u>Example of calculation</u>	**(3)**
	- calculation of difference in x and difference in y **(1)**	0.00337 – 0.00317 = 0.00020 −5.75 + 4.39 = (−) 1.36 M1 could be subsumed in M2	
	- calculation of gradient **(1)**	−1.36 ÷ 0.00020 = − 6800 (K) M2 could be subsumed in M3 Allow gradient in range of −6200 to −7000	
	- calculation of activation energy to 2 or 3 SF, including units **(1)**	6800 × 8.31 = 56508 = (+) 56500 / 57000 J mol^{-1} Accept (+) 56.5 / 57 kJ mol^{-1} Final correct answer with some working scores 3 marks Allow TE from M1 to M2 Allow TE from M2 to M3 if final answer is positive	

Question Number	Answer	Additional Guidance	Mark
4(b)(ii)	• no, as value for ln (collision factor) is the y intercept when x = 0	Allow graph shows ln(rate) which may / will not give the same y intercept as ln*k* Allow possible proof based on calculation of ln(collision factor) using Arrhenius equation (e.g. value of 17, based on a gradient of −6800)	**(1)**

(Total Marks for Question 4 = 14 marks)

SECTION B

Answer ALL the questions. Write your answers in the spaces provided.

14: This question is about nitrosyl chloride, NOCl, which is a yellow gas.
Nitrosyl chloride decomposes into yellow-green chlorine, Cl_2, and colourless nitric oxide, NO, as shown.

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

(a) A mixture of nitrosyl chloride, chlorine and nitric oxide was placed in a sealed container and allowed to reach equilibrium.

Explain what you would expect to **see** when the pressure of the equilibrium mixture is increased.

(2)

....

....

....

....

....

(b) 0.250 mol of nitrosyl chloride in a 500 cm^3 sealed container was heated to 200 °C. At equilibrium there was 0.016 mol of chlorine in the mixture.

(i) Write the expression for the equilibrium constant K_c.

(1)

(ii) Complete the table using the equilibrium equation and the data.

(2)

Substance	NOCl	NO	Cl_2
Initial mol	0.250	0	0
Equilibrium mol			0.016
Concentration / mol dm^3			

(iii) Using your answers from (b)(i) and (b)(ii), calculate the equilibrium constant, K_c.
Give your answer to an appropriate number of significant figures and include units.

(3)

(iv) When the temperature is reduced, the value of the equilibrium constant, K_c, becomes smaller.

Explain what can be deduced about the nature of the reaction.

(2)

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(Total for Question 14 = 10 marks)

18: This question is about the kinetics of the catalytic decomposition of hydrogen peroxide, H_2O_2, using manganese(IV) oxide as a catalyst.

The equation for the decomposition is shown.

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

In an experiment, 10 cm^3 of hydrogen peroxide solution was added to 150 cm^3 of distilled water. A small amount of manganese(IV) oxide granules was added and the clock started.

Every 5 minutes, 10 cm^3 samples of the reaction mixture were withdrawn using a pipette and transferred to a conical flask.

The samples were then acidified with dilute sulfuric acid and titrated with potassium manganate(VII) solution. The equation for the titration is shown.

$$2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$$

The results of the experiment are given in the table.

Time / min	0	5	10	15	20	25	30
Volume of manganate(VII) / cm^3	32.5	24.8	18.9	13.9	10.5	8.1	6.5

(a) (i) The reaction in the sample stops immediately on removal from the reaction mixture.

Suggest why this occurs.

(1)

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....

(ii) State why it is not necessary to calculate the concentration of hydrogen peroxide solution when trying to deduce the order of reaction with respect to hydrogen peroxide.

(1)

....

....

....

(iii) Plot a graph of the volume of potassium manganate(VII) solution against time.

(3)

(iv) Use your graph to show that the reaction is first order with respect to hydrogen peroxide. You must show your working on the graph.

(3)

(b) Two possible mechanisms have been suggested by students carrying out this reaction.

Mechanism 1

Step 1 $2H_2O_2(aq) \rightarrow [H_4O_4](aq)$ slow
transition state

Step 2 $[H_4O_4](aq) \rightarrow 2H_2O(l) + O_2(g)$ fast

Mechanism 2

Step 1 $H_2O_2 \rightarrow 2OH$ slow

Step 2 $H_2O_2 + OH \rightarrow H_2O + HO_2$ fast

Step 3 $HO_2 + OH \rightarrow H_2O + O_2$ fast

Explain whether or not these mechanisms are consistent with the reaction being first order.

(2)

(Total for Question 18 = 10 marks)

TOTAL FOR SECTION B = 51 MARKS

SECTION C

Answer ALL the questions. Write your answers in the spaces provided.

19: This question is about some copper compounds.

(a) Crystals of hydrated copper(II) sulfate, $CuSO_4{\bullet}5H_2O$, lose water when heated, forming anhydrous copper(II) sulfate, $CuSO_4$.

$$CuSO_4{\bullet}5H_2O(s) \rightarrow CuSO_4(s) + 5H_2O(l)$$

Substance	$CuSO_4{\bullet}5H_2O(s)$	$CuSO_4(s)$	$H_2O(l)$
Standard enthalpy of formation, $\Delta_f H^\ominus$ / $kJ\,mol^{-1}$	−2279.6	−771.4	−285.8
Standard molar entropy, $S^\ominus$ / $J\,K^{-1}\,mol^{-1}$	300.4	109.0	69.9

(i) Using the data in the table, calculate the standard enthalpy change, $\Delta_r H^\ominus$, for this reaction.

(2)

(ii) Using the data in the table, calculate the standard molar entropy change, $\Delta S^\ominus_{system}$, for this reaction.

(2)

(iii) Using your answers from (a)(i) and (a)(ii), calculate the **lowest** temperature at which hydrated copper(II) sulfate will decompose.

(3)

(b) Hydrated copper(II) sulfate is soluble in water. A student carried out an experiment to determine its enthalpy change of solution.

100 g of distilled water was placed in a polystyrene cup and the temperature recorded.

21.36 g of hydrated copper sulfate was added to the distilled water, the mixture stirred, and the minimum temperature recorded.

Using this data, the student's calculated enthalpy change of solution was +12.3 kJ mol^{-1}.

Calculate the temperature change in this experiment.

[specific heat capacity of the solution is 3.7 J g^{-1} °C
total mass of solution = 121.36 g
molar mass of $CuSO_4{\bullet}5H_2O$ = 249.6 g mol^{-1}]

(4)

(c) Copper(II) chloride, $CuCl_2$, is another copper compound that is soluble in water. It is possible to calculate the enthalpy change of solution, $\Delta_{sol}H$, using a Hess cycle and the lattice energy and enthalpy changes of hydration, $\Delta_{hyd}H$.

(i) Explain what is meant by the term **enthalpy change of hydration**.

(2)

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....

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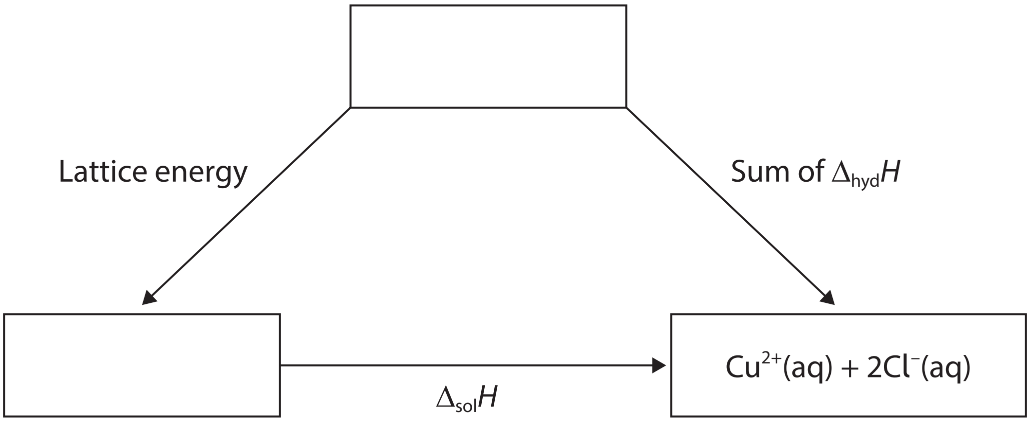
(ii) Complete the Hess cycle by filling in the empty boxes.

(1)



(iii) Complete the expression for the enthalpy change of solution using the enthalpy changes of hydration and lattice energy.

(1)

$\Delta_{sol}H =$

(iv) The lattice energy of copper(II) chloride is −2811 kJ mol^{-1}.
Use this value, the data in the table, and your expression in (c)(iii) to calculate the enthalpy change of solution.

(2)

Ion	Enthalpy change of hydration / kJ mol^{-1}
Cu^{2+}	−2100
Cl^{-}	−378

(v) The enthalpy change of hydration of Cu^+ is –593 kJ mol^{-1}.
Explain why the hydration enthalpy of Cu^+ is much less exothermic than Cu^{2+}.

(2)

(Total for Question 19 = 19 marks)

TOTAL FOR SECTION C = 19 MARKS
TOTAL FOR PAPER = 90 MARKS

Section B

Question Number	Answer	Additional Guidance	Mark
14(a)	An explanation that makes reference to the following points: • (after initially getting darker) the mixture would turn yellower / more yellow **(1)** • (so eqm shifts left / favours the LHS as there are) fewer molecules/ mol on the LHS **(1)**	Allow less green Allow more yellow gas Allow darker yellow Allow just turns yellow Ignore initial colour Allow mole ratio2:3 and this may be shown on the equation Allow reverse argument Do not award eqm shifts right There is no TE	**(2)**

Question Number	Answer	Additional Guidance	Mark
14(b)(i)	An answer that makes reference to the following point: • $(K_c =) \frac{[NO]^2[Cl_2]}{[NOCl]^2}$	Ignore state symbols Do not award round brackets/ pp Do not award if the ^{2} is inside the bracket	**(1)**

<table>
<tr><th>Question Number</th><th>Answer</th><th>Additional Guidance</th><th>Mark</th></tr>
<tr><td>14(b)(ii)</td><td>An answer that makes reference to the following points:
• second row correct (1)
• third row correct (1)</td><td><table>
<tr><th>Substance</th><th>NOCl</th><th>NO</th><th>Cl_2</th></tr>
<tr><td>Initial mol</td><td>0.250</td><td>0</td><td>0</td></tr>
<tr><td>Equilibrium mol</td><td>0.218</td><td>0.032</td><td>0.016</td></tr>
<tr><td>Concentration / mol dm^{-3}</td><td>0.436</td><td>0.064</td><td>0.032</td></tr>
</table>
Allow TE on second row</td><td>(2)</td></tr>
</table>

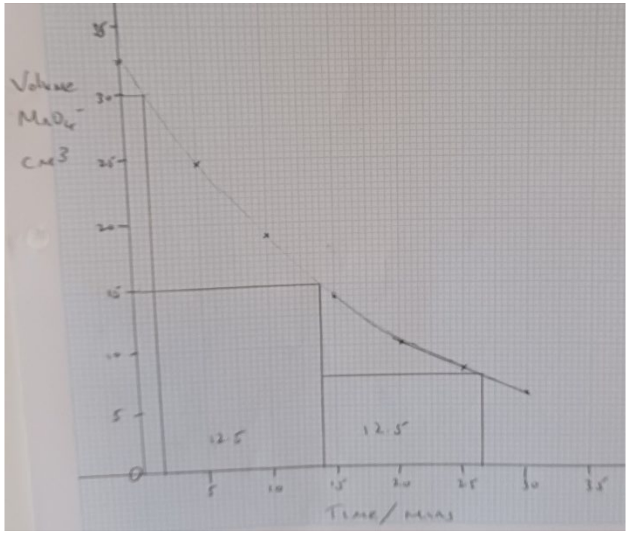
Question Number	Answer	Additional Guidance	Mark
14(b)(iii)	• correct use of K_c expression **(1)** • correct answer **(1)** • with units and 1 to 3 SF **(1)**	Example of calculation: $(0.064)^2 \times 0.032 \div 0.436^2$ 6.8950×10^{-4} / 0.00068950 6.9×10^{-4} / 6.90×10^{-4} / 7×10^{-4} mol dm^{-3} Allow TE from *Kc* expression in (b)(i) and numbers in (b)(ii)	**(3)**

Question Number	Answer	Additional Guidance	Mark
14(b)(iv)	An explanation that makes reference to the following points: • (forward) reaction is endothermic/ ΔH is positive **(1)** • (at the lower temperature) reaction moves in the exothermic direction/backwards/to the left (making the value of K_c smaller) **(1)**	Standalone marks Allow reverse argument if reverse reaction is stated Allow equilibrium shifts left Allow favours instead of moves/shifts Allow makes more reactants/NOCl	**(2)**

(Total for Question 14 = 10 marks)

Question Number	Answer	Additional Guidance	Mark
18(a)(i)	An answer that makes reference to the following point: • the reaction mixture is separated from the catalyst	Allow any indication that the catalyst is no longer in contact with the solution. Allow the catalyst is removed Allow granules for catalyst Ignore reference to dilution/ quenching	**(1)**

Question Number	Answer	Additional Guidance	Mark
18(a)(ii)	An answer that makes reference to the following point: • the concentration (of hydrogen peroxide is directly) proportional to the volume of (potassium) manganate (VII)	Allow they react in a specific ratio / 5:2 ratio Allow the other way round Allow it is proportional to the volume of manganate	**(1)**

Question Number	Answer	Additional Guidance	Mark
18(a)(iii)	• axes labelled with time and mins on x axis and volume ($KMnO_4$) and cm^3 on y axis **(1)** • suitable scale so the points cover at least 50% of the graph in both directions **(1)** • points plotted correctly to (+/−) square **and** smooth **curve** through points **(1)**	Example of graph:  Ignore extension beyond 30 minutes as long as it follows the curve	**(3)**

Question Number	Answer	Additional Guidance	Mark
18(a)(iv)	An answer that makes reference to the following points: • (first order as) the half-life is constant/similar **(1)** • two half-lives drawn on the graph **(1)** • two stated half-lives values within the range of 11.5 - 13.5 (mins) **(1)**		**(3)**

Question Number	Answer	Additional Guidance	Mark
18(b)	An answer that makes reference to the following points: • the slow step/rate determining step involves two molecules/mol (of hydrogen peroxide) so the mechanism is not consistent with being a first order reaction **(1)** • the slow step/rate determining step involves one molecule/mol (of hydrogen peroxide) so the mechanism is consistent with being a first order reaction **(1)**	Allow the slow step/rate determining step involves two molecules/mol (of hydrogen peroxide) so not first order/ is second order Allow the slow step/rate determining step involves two H_2O_2 so not first order/ is second order Allow the slow step/rate determining step involves one molecule/mol (of hydrogen peroxide) so is first order Allow the slow step/rate determining step involves one H_2O_2 so is first order If they state that mechanism 1 is second order and mechanism 2 first order (so consistent) award one mark if no other marks have been scored. This can also be shown by two rate equations. Ignore any reference to S_N1, S_N2 etc	**(2)**

(Total for Question 18 = 10 marks)
TOTAL FOR SECTION B = 51 MARKS

Section C

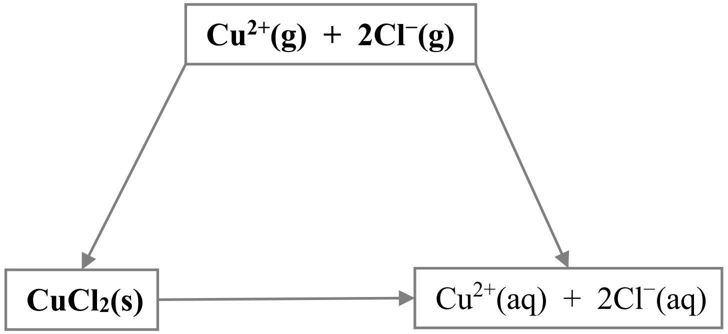
Question Number	Answer	Additional Guidance	Mark
19(a)(i)	• correct use of data **(1)** • correct answer **(1)**	Example of calculation: -285.8×5 (+) -771.4 (–) -2279.6 (kJ mol^{-1}) (+)79.2 / 79 (kJ mol^{-1}) Correct answer with or without working scores 2 TE M1	**(2)**

Question Number	Answer	Additional Guidance	Mark
19(a)(ii)	• $\sum S$ products **(1)** • $\Delta S = \sum S$ products $- \sum S$ reactants **(1)**	Example of calculation: S = products $(5 \times 69.9) + 109.0 = 458.5$ (J K^{-1} mol^{-1}) $458.5 - 300.4 =$ (+)158.1 / 158 / 160 (J K^{-1} mol^{-1}) TE on M1	**(2)**

Question Number	Answer	Additional Guidance	Mark
19(a)(iii)	• rearrangement of expression **(1)** • numbers inserted into rearranged expression **(1)** • calculation of temperature **(1)**	Example of calculation: $T= \frac{\Delta H}{\Delta S_{\text{system}}}$ $T = \frac{79.2 \times 1000}{158.1}$ 500.95(K) / 500.9(K) / 501(K) / 227.95ºC / 228ºC K is in brackets but if converted to ºC the units must be seen	**(3)**

Question Number	Answer	Additional Guidance	Mark
19(b)	• calculation of mol of copper sulfate **(1)** • calculation of joules **(1)** • rearrangement to give ΔT **(1)** • correct answer **(1)**	<u>Example of calculation:</u> 21.36 ÷ 249.6 = 0.085577 (mol) 12.3 × 0.085577 × (1000) = 1052.6 (J) or 1.0526 (kJ) ΔT = 1052.6 (J) ÷ (121.36 × 3.7) = (–) 2.344 / 2.3 / 2(°C) Ignore SF Ignore sign Correct answer without working scores 4	**(4)**

Question Number	Answer	Additional Guidance	Mark
19(c)(i)	An explanation that makes reference to the following points: • enthalpy change when 1 mol of **gaseous** ions **(1)** • **completely** hydrated (in water)/ forms an infinitely dilute solution (with water)/ dissolve until there is no further temperature or heat change **(1)**	Do not award any reference to heat needed or energy required. Allow is **completely** dissolved (in water) Allow dissolved in water to produce a 1.0 mol dm^{-3} solution Ignore any reference to standard conditions Do not award dissolved in 1 mol of water	**(2)**

Question Number	Answer	Additional Guidance	Mark
19(c)(ii)	• both bold boxes correct scores 1		**(1)**

Question Number	Answer	Additional Guidance	Mark
19(c)(iii)	• $\Delta_{sol}H$ = (sum of) $\Delta_{hyd}H$ − Lattice energy OR $\Delta_{sol}H$ = − Lattice energy + (sum of) $\Delta_{hyd}H$	Allow $\Delta_{hyd}H$ (Cu^{2+}) + 2$\Delta_{hyd}H$ (Cl^-) for $\Delta_{hyd}H$	(1)

Question Number	Answer	Additional Guidance	Mark
19(c)(iv)	• calculation of enthalpy of hydration of copper(II) chloride **(1)** • calculation of enthalpy of solution **(1)**	Example of calculation −2100 + − (378 × 2) = −2856 (kJ mol^{-1}) −2856 (−) −2811 = −45 (kJ mol^{-1}) (+) 45 (kJ mol^{-1}) scores 1 Allow TE from M1 to M2 Ignore SF except 1SF Correct answer with or without working scores 2	(2)

Question Number	Answer		Additional Guidance	Mark
19(c)(v)	- Cu^+ less highly charged/ less positive (than Cu^{2+})	(1)	Allow Cu^+ (has a) is larger (ionic radius) (than Cu^{2+}) Allow Cu^+ (has a) lower charge density (than Cu^{2+}) Do not award reference to atoms	(2)
	- less strong (electrostatic) forces of attraction with **water** (so less energy is released when the ions are hydrated)	(1)	Allow there is a weaker attraction between the Cu^+ ions and **water** molecules. Allow weaker bonds with **water** Accept weaker ion- dipole forces with **water** Do not award intermolecular forces Do not award if there is any indication of energy required Allow reverse argument for both points	

(Total for Question 19 = 19 marks)

TOTAL FOR SECTION C = 19 MARKS
TOTAL FOR PAPER = 90 MARKS

3: A 'clock' reaction may be used to determine the activation energy for the reduction of peroxodisulfate(VI) ions, $S_2O_8^{2-}$(aq), by iodide ions, I^-(aq).

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

A small amount of thiosulfate ions, $S_2O_3^{2-}$(aq), is added to the reaction mixture, which also contains some starch indicator.

$$2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

Procedure

Step **1** Prepare a water bath by heating a half-full beaker of water to approximately 50 °C.

Step **2** Using a burette, add 10.0 cm^3 of 0.020 mol dm^{-3} $S_2O_8^{2-}$(aq) ions into a boiling tube.

Step **3** Into a second boiling tube, use separate burettes to add 5.0 cm^3 of 0.50 mol dm^{-3} I^-(aq) ions, 5.0 cm^3 of 0.010 mol dm^{-3} $S_2O_3^{2-}$(aq) ions, and 2.5 cm^3 of 0.2% starch solution.

Step **4** Place both boiling tubes in the water bath and add a thermometer to each. When the temperatures of the two solutions are the same as the water bath, pour the contents of the second boiling tube into the first, stir and start a timer.

Step **5** Stop the timer when the colour changes and record the time, *t*. The reciprocal of the time, 1 / *t*, is proportional to the initial rate.

Step **6** Repeat the experiment at several temperatures between 45 °C and 25 °C.

(a) Explain why thiosulfate ions, $S_2O_3^{2-}$(aq), are added to the reaction mixture.

(2)

....

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....

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(b) Explain why a burette, and not a measuring cylinder, is used to add the starch solution in Step **3**, even though the concentration of starch indicator does not need to be exactly the same at each temperature.

(2)

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....

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....

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....

(c) State the colour change in Step **5**.

(2)

Colour change from .... to ....

(d) Some results from the experiment are shown.

T / °C	T / K	$(1/T)$ / K^{-1}	Time, t / s	$(1/t)$ / s^{-1}	ln (1 / t)
	322	0.00311	33	0.0303	–3.50
43			47	0.0213	–3.85
36	309	0.00324	72	0.0139	–4.28
31	304	0.00329			–4.60
25	298	0.00336	147	0.00680	

(i) Complete the table.

(3)

(ii) The experimental data was plotted on a graph of ln (1 / t) against 1 / T, giving a straight line with gradient, $m = -6045$ K.

Calculate the activation energy, E_a, for this reaction, in kJ mol^{-1}, using this result.

$$\ln(1/t) = -\frac{E_a}{R} \times \frac{1}{T} + \text{constant} \qquad R = 8.31\ \text{J mol}^{-1}\ \text{K}^{-1}$$

(1)

(Total for Question 3 = 10 marks)

Question Number	Answer	Additional Guidance	Mark
3(a)	An explanation that makes reference to the following points: • to react with iodine/I_2 **(1)** • to delay the colour change **(1)**	M1 and M2 are independent marks Allow to remove/reduce iodine/I_2 Allow to convert iodine/I_2 to iodide/I^- Allow so iodine/I_2 reacts with starch after forming $S_4O_6^{2-}$ Ignore just as a reducing agent Do not award to react with iodide/I^- Allow colour forming for colour change Allow to prevent an immediate colour change Allow so colour changes after thiosulfate/$S_2O_3^{2-}$ is used up Allow so colour changes after $S_4O_6^{2-}$ formed Allow so colour changes after a known amount of iodine/I_2 formed Ignore any reference to reaction rate Ignore to quench/stop reaction Ignore to make colour change more obvious Ignore end-point for colour change	**2**

Question Number	Answer	Additional Guidance	Mark
3(b)	An explanation that makes reference to the following points: • to keep the (total) volume the same **(1)** • (so) concentration (of $S_2O_8^{2-}$/I^-/ $S_2O_3^{2-}$/reactants) remains constant **(1)**	Ignore any reference to colour change Allow so volume of starch is the same Allow as some solution would remain in the measuring cylinder Allow just more accurate/precise Allow just smaller (percentage) uncertainty Ignore starch must be added drop by drop/slowly Ignore just easier to use / easier to add 2.5 cm^3 Ignore measuring cylinder cannot measure small volumes/2.5 cm^3 Allow as concentration is (inversely) proportional to volume Ignore so temperature is the only variable Do not award so concentration of starch/iodine remains constant Do not award so amount/moles remains constant	**2**

Question Number	Answer	Additional Guidance	Mark
3(c)	An answer that makes reference to the following points: • (from) colourless **(1)** • (to) blue-black **(1)**	Ignore clear Do not award any other answer, eg yellow Allow blue or black Do not award pale or light Do not award any other colour, eg yellow/brown Reverse colour change scores (1)	**2**

<table>
<tr><th>Question Number</th><th>Answer</th><th>Additional Guidance</th><th>Mark</th></tr>
<tr><td>3(d)(i)</td><td>

- any two or three scores **(1)**
- any four or five scores **(2)**
- all six scores **(3)**

</td><td>Penalise incorrect SF once only

Example of completed table:
<table>
<tr><th>T / °C</th><th>T / K</th><th>$(1/T)$ / K^{-1}</th><th>Time, t / s</th><th>$(1/t)$ / s^{-1}</th><th>$\ln(1/t)$</th></tr>
<tr><td><u>49</u></td><td>322</td><td>0.00311</td><td>33</td><td>0.0303</td><td>−3.49</td></tr>
<tr><td>43</td><td><u>316</u></td><td><u>0.00316</u></td><td>47</td><td>0.0213</td><td>−3.85</td></tr>
<tr><td>36</td><td>309</td><td>0.00324</td><td>72</td><td>0.0139</td><td>−4.28</td></tr>
<tr><td>31</td><td>304</td><td>0.00329</td><td><u>99</u></td><td><u>0.0101</u></td><td>−4.60</td></tr>
<tr><td>25</td><td>298</td><td>0.00336</td><td>147</td><td>0.00680</td><td><u>−4.99</u></td></tr>
</table>
Allow TE for $1/T$ at 43°C from T / K value
Allow TE for Time, t at 31°C from (1/t) value</td><td>3</td></tr>
</table>

Question Number	Answer	Additional Guidance	Mark
3(d)(ii)	• activation energy (in kJ mol^{-1})	Example of calculation: $E_a = -(-6045) \times 8.31 = 50234$ $= (+)50.234$ (kJ mol^{-1}) Allow (+)50 234 **J mol^{-1}** Ignore SF Do not award negative sign Do not award incorrect units	**1**

(Total for Question 3 = 10 marks)